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^{77}Se NMR study of the electronic instability in $TiSe_2$

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Nuclear-magnetic-resonance data are reported for ^{77}Se in polycrystalline $TiSe_2$ over the temperature range 1.5 –342 K. The isotropic Knight shift exhibits a pronounced decrease with decreasing temperature, beginning roughly 40 K above the second-order phase transition ($T_0 = 202$ K). Above T_0 an axially symmetric anisotropic Knight shift is observed, whereas a nonaxial component develops gradually as the temperature is lowered below T_0. At room temperature the Knight shift components are $K_{iso} = (0.111 \pm 0.005)\%$, $K_{ax} = (0.0105 \pm 0.0010)\%$; the components at 77 K are $K_{iso} = (0.082 \pm 0.005)\%$, $K_{ax} = (0.0130 \pm 0.0010)\%$, and $K_{asym} = (0.0120 \pm 0.0010)\%$. The shift components are nearly independent of temperature below 100 K. Measurements of the spin-lattice relaxation times show a sharp decrease in $(T_1T)^{-1}$ consistent with that of the isotropic Knight shift. Analysis of the results indicates that a small admixture of *s* character at the Se sites is essentially eliminated by Fermi-surface modifications associated with the phase transition. A pronounced but poorly understood peak in $(T_1T)^{-1}$ is observed near 10 K.

I. INTRODUCTION

The semimetallic layered compound $TiSe_2$ has received considerable recent attention, primarily because of its second-order structural transition at 202 K. The transition is of particular interest because of its similarity to those occurring in several *metallic* layered dichalcogenides of group-V*b* transition metals.[1] These have been found to be driven by the onset of electronic charge-density waves.[2] It has not been established whether the transition in the semimetal $TiSe_2$ is also due to a charge-density wave[3,4] or, for example, is driven by a soft-phonon mode whose effect is enhanced by the conduction electrons.[5]

A number of recent studies have been concerned with the structural changes occurring at the phase transition. Electron- and neutron-diffraction experiments have established that the transition leads to a doubling of the hexagonal unit cell in both directions.[3,4,6–8] In addition, weak incommensurate spots have been observed in electron diffraction in the range 110–170 K.[4,6] The origin of these spots and, in particular, the explanation of their disappearance on cooling remain unknown.

The electronic-transport properties and the magnetic susceptibility were investigated by DiSalvo, Moncton, and Waszczak.[3] Their analysis of the conductivity, thermopower, and Hall coefficient confirmed the semimetallic nature of stoichiometric $TiSe_2$ and they estimated a carrier concentration in the range $(1-3)\times10^{20}$ cm^{-3}. The same conclusion was reached by Bachrach, Skibowski, and Brown from their angle-resolved photoemission studies of nonstoichiometric samples.[9] Comparison of the band structure of[10] $TiSe_2$ with those of the isostructural compounds[11] 1*T*-TaS_2 and 1*T*-HfS_2 shows that the electrons are derived mainly from Ti *d* states while the holes are found in the Se *p* band. The magnetic and electronic properties are strongly affected by the transition and the data indicate a reduction in carrier density in the low-temperature phase.[3] Consideration of these electronic changes together with the low-temperature atomic displacements has led to an interpretation of this transition in terms of a commensurate charge-density wave involving nesting of electrons at the *L* point of the Brillouin zone with holes at Γ.[3,4] However an alternative model of the transition has been proposed by White and Lucovsky who interpreted their optical-reflectivity data as evidence for a soft-phonon-driven antiferroelectric transition.[5]

The present study was undertaken in the expectation that NMR data would further illuminate the electronic structure of $TiSe_2$ and the nature of the phase transition. We have measured the ^{77}Se Knight shift, both its isotropic and anisotropic components, over a temperature range 4.2–342 K. The nuclear spin-lattice relaxation time (T_1) was measured from 1.5 to 298 K. Our work represents the first comprehensive NMR investigation of $TiSe_2$; the ^{77}Se Knight shift at room temperature was reported previously by Silbernagel and Gamble as part of a survey of the layered diselenides.[12]

II. EXPERIMENTAL DETAILS

A principal experimental difficulty with ^{77}Se NMR is the relatively poor sensitivity resulting from the low spin ($I = \frac{1}{2}$) and, particularly, the low natural abundance (7.5%) of this isotope. In the present work, this problem was greatly alleviated by the use of Se enriched to 94.4% ^{77}Se. Our powdered sample of TiSe$_2$ was prepared as described by DiSalvo *et al.*,[3] using enriched Se obtained from the U.S. ERDA.[13] The preparation conditions (580 °C in a slight excess of Se) corresponded to those used in earlier investigations of the electrical transport and magnetic properties and for neutron-scattering experiments.[3] After preparing the compound we sealed the sample in a quartz ampoule containing a He atmosphere.

Pulsed NMR measurements were made at 13.6 MHz using a coherent spectrometer. The presence of an anisotropic Knight shift led to complex free-induction-decay shapes. However, the line shapes could be displayed in a convenient form by sweeping the magnetic field while integrating the free-induction decay with a boxcar integrator in the manner described by Clark.[14] The lifetime of the shortest component of the free-induction decay ($T_2^* \sim 30$ μsec) was sufficiently long compared with the apparatus dead time (5 μsec) that nearly distortion-free absorption line shape displays could be obtained (Fig. 1).

Values of the magnetic field at resonance for ^{77}Se were determined from the frequency of the ^{2}H resonance in D$_2$O in the same field. The reference value for the Knight shift was the ratio of frequencies for ^{77}Se and ^{2}H [$\nu(^{77}\text{Se})/\nu(^2\text{H}) = 1.244101 \pm 0.000046$] measured by Silbernagel and Gamble in various aqueous reference solutions such as the H$_2$SeO$_4$.[12] The estimated experimental error in the absolute values of our Knight shift results is ±0.005% of the applied field, while the relative error for measurements at different temperatures is about ±0.001%.

Spin-lattice relaxation times (T_1) were measured in the conventional manner with either a saturating comb of pulses or a single 180° pulse, followed by a 90° sampling pulse and free-induction decay. The experimental uncertainty was typically about ±7%.

Variable temperature control was achieved with a gas-flow system using N$_2$ gas for temperatures above 100 K and He gas for lower temperatures. The temperature stability and the accuracy of the temperature measurements using copper-Constantan and gold(iron)-chromel thermocouples gave an overall estimated error of ±2 K for the sample temperature determinations.

III. EXPERIMENTAL RESULTS AND ANALYSIS

A. Knight shift

The observed ^{77}Se absorption line shape is reproduced in Fig. 1 for representative temperatures above and below the phase transition. Above T_0, the line shape shows the characteristic powder pattern produced by an anisotropic Knight shift when the nuclei occupy sites of axial symmetry.[15] The line shape was independent of temperature in the range 226–342 K. As the sample was cooled below T_0, the line shape began to change progressively, eventually reaching a new temperature-independent profile below about 100 K. The low-temperature line shape is recognizable as characteristic of an anisotropic Knight shift in nonaxial symmetry. This line shape is necessarily of magnetic origin since the electric quadrupole interaction vanishes for nuclear spin $\frac{1}{2}$.

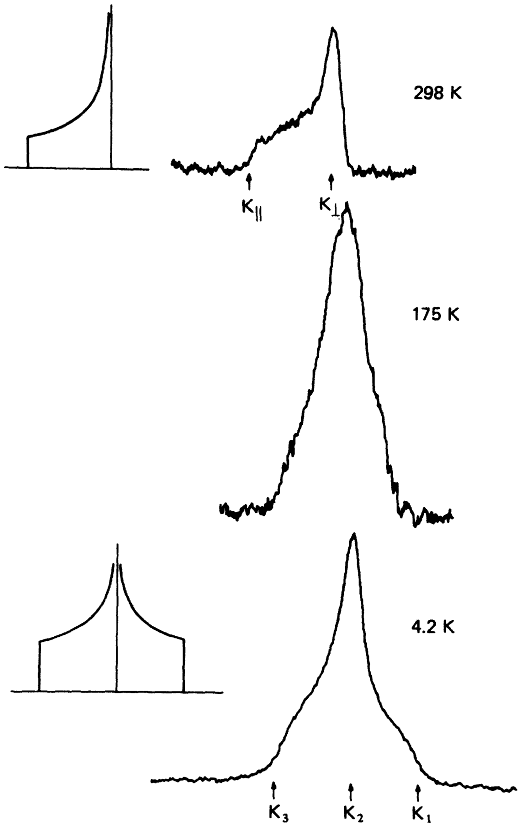

FIG. 1. ^{77}Se-absorption line shapes in TiSe$_2$ at representative temperatures above and below the phase transition ($T_0 = 202$ K). The high-temperature (axial) and low-temperature (nonaxial) Knight shift components are indicated by arrows. Theoretical line shapes in the absence of dipolar broadening are shown on the left-hand side for axial and nonaxial symmetry.

Before discussing the Knight shifts in detail, we recall the parameters used to characterize the isotropic and anisotropic shifts. For a single crystal, the total shift can be expressed in the following form[15]:

$$K(\Theta, \Phi) = K_{\text{iso}} + K_{\text{ax}}(3\cos^2\Theta - 1) + K_{\text{asym}}\sin^2\Theta\cos 2\Phi \ , \qquad (1)$$

where (Θ, Φ) describe the orientation of the principal axes of the shift tensor with respect to the magnetic field. Now the experimental line shapes can be parametrized in terms of three shift values K_1, K_2, and K_3 as indicated in Fig. 1. For axial symmetry there are two parameters $K_\parallel \equiv K_3$ and $K_\perp \equiv K_1 = K_2$. When Eq. (1) is averaged over all values of Θ and Φ, as appropriate for a powder, the resulting line shape yields the following correspondences:

$$K_{\text{iso}} = \tfrac{1}{3}(K_1 + K_2 + K_3) \underset{\text{axial}}{\rightarrow} \tfrac{1}{3}(2K_\perp + K_\parallel) \ , \quad \text{(2a)}$$

$$K_{\text{ax}} = \tfrac{1}{3}(K_3 - \tfrac{1}{2}K_2 - \tfrac{1}{2}K_1) \underset{\text{axial}}{\rightarrow} \tfrac{1}{3}(K_\parallel - K_\perp) \ , \quad \text{(2b)}$$

$$K_{\text{asym}} = \tfrac{1}{2}(K_2 - K_1) \underset{\text{axial}}{\rightarrow} 0 \ . \quad \text{(2c)}$$

The values of K_{iso}, K_{ax}, and K_{asym} discussed below were obtained by means of Eqs. (2a)–(2c) from values of K_1, K_2, and K_3 given by the peaks and "shoulders" in experimental traces such as those shown in Fig. 1.

1. Isotropic Knight shift

The isotropic Knight shift K_{iso} is shown as a function of temperature in Fig. 2. The most notable features of the temperature dependence are a sharp drop with decreasing temperature beginning at about 240 K and a nearly temperature-independent value observed below about 100 K. [A decrease in the shift near 200 K has also been observed by Silbernagel and Gamble in a preliminary experiment (private communication)]. Note that the shift begins to decrease well above the transition temperature T_0. Less obvious features of the temperature dependence are a slight rise in K_{iso} below 20 K and a very small "bump" between 120 and 160 K. It should be noted that both of these latter "effects" lie just at the limit of our estimated experimental error.

The value of K_{iso} at 298 K is 0.107 ± 0.005% which agrees well with the value 0.111 ± 0.005% given by Silbernagel and Gamble.[12] However, we should point out that those authors did not describe their results in terms of an anisotropic Knight shift and, hence, their definition of the Knight shift may be slightly different from that which we have used to obtain K_{iso}.

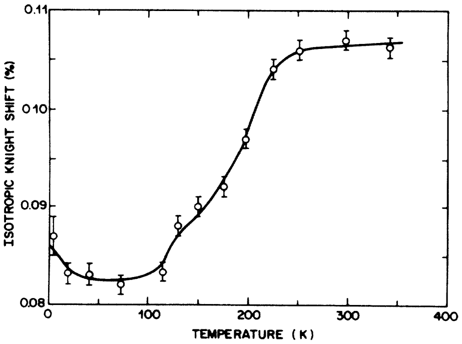

FIG. 2. Isotropic Knight shift vs temperature for ^{77}Se in TiSe$_2$

The isotropic Knight shift may be expressed as the sum of several contributions,

$$K_{\text{iso}} = K_{\text{iso}}^{\text{cp}} + K_{\text{iso}}^{\text{VV}} - \sigma_{\text{chem}} + K_{\text{iso}}^{s} \ , \quad (3)$$

where $K_{\text{iso}}^{\text{cp}}$ and $K_{\text{iso}}^{\text{VV}}$ are, respectively, the p-electron core polarization and Van Vleck orbital terms, K_{iso}^{s} is the s-electron contact term, and σ_{chem} is the chemical shift. The negative sign before σ_{chem} in Eq. (3) reflects the conventional definition of the chemical shift as a reduction of the local magnetic field, whereas a positive Knight shift indicates an increased local field. To the extent possible, we shall identify the terms in Eq. (3) providing the dominant temperature-dependent and temperature-independent shift contributions.

An immediate indication of the importance of $K_{\text{iso}}^{\text{VV}}$ and σ_{chem} is provided by comparison of the magnitude of K_{iso} with values recently reported for ^{77}Se in TaSe$_2$ and NbSe$_2$ by Borsa and Torgeson.[16] Analyses of the axially symmetric shifts in those systems yielded $K_{\text{iso}} = 0.167\%$ (TaSe$_2$) and $K_{\text{iso}} = 0.338\%$ (NbSe$_2$). At first sight it seems somewhat surprising that K_{iso} is nearly as large in TiSe$_2$ as in TaSe$_2$ since the carrier density is much higher in the latter compound. However the terms $K_{\text{iso}}^{\text{VV}}$ and $-\sigma_{\text{chem}}$ do not depend on the density of states at the Fermi level and the relatively large value of K_{iso} in TiSe$_2$ therefore suggests that one (or both) of these terms makes a major positive contribution to K_{iso}.

An additional indication of the source of the shift can be obtained from a comparison of the temperature dependence of K_{iso} with that of the total magnetic susceptibility. This is illustrated in Fig. 3 where K_{iso} is

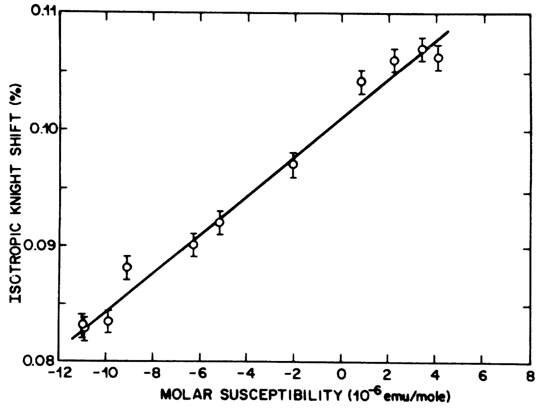

FIG. 3. Isotropic ^{77}Se Knight shift vs molar susceptibility for powdered TiSe$_2$ (Ref. 3). The data span a temperature range 40–342 K.

plotted against the molar susceptibility χ_m of a powder sample.[3] Although the scatter exceeds our estimated error, the linear fit is good enough to show that the temperature dependences of $K_{\rm iso}$ and χ_m are closely related.

Now the slope of a K-vs-χ plot can often be used to determine the hyperfine coupling corresponding to the temperature-dependent parts of the shift and susceptibility.[17] In the present case, unfortuantely, we do not know how the total susceptibility is shared between the Ti and Se sites. Thus, while we can readily determine the slope $dK_{\rm iso}/d\chi_m = 16.8$ mol/emu, we have no straightforward way of determining $dK_{\rm iso}/d\chi_{\rm Se}$ as needed to get a hyperfine field value. The situation is further complicated by the fact that a significant part of the temperature dependence of χ_m is due to anisotropic contributions,[3] and hence not directly related to $K_{\rm iso}$. Because of this, and the likelihood that $\chi_{\rm Ti}$ is somewhat larger than $\chi_{\rm Se}$, we estimate that $d\chi_{\rm Se}^{\rm iso}/dT \lesssim (0.1)\, d\chi_m/dT$. The slope of the $K_{\rm iso}$-vs-χ_m plot then indicates a hyperfine field in excess of 1 MG/μ_B, a value which could only result from an s-electron component of the susceptibility. We are thus led to the tentative conclusion that the temperature dependence of $K_{\rm iso}$ is due mainly to the term $K_{\rm iso}^{s}$, while the sum $(K_{\rm iso}^{\rm VV} - \sigma_{\rm chem})$ provides a relatively large positive shift which is not strongly dependent on temperature. Additional evidence for this decomposition will be presented in connection with the analysis of our T_1 data.

2. *Anisotropic Knight shift*

The crystal structure of $TiSe_2$ above T_0 is that of CdI_2 consisting of layered Se-Ti-Se "sandwiches" separated by a Van der Waals gap. Within each layer the atoms form a two-dimensional hexagonal array and the stacking is such that the Ti coordination is essentially octahedral (the so-called $1T$ modification). The Se coordination, of primarily interest in the present work, is shown in Fig. 4. The site symmetry is trigonal and this is responsible for the axial character of the anisotropic Knight shift.

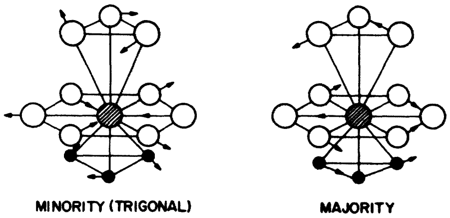

FIG. 4. Se coordination in $TiSe_2$. Large circles represent Se atoms and small circles represent Ti atoms. Arrows indicate directions of atomic displacements for the minority (trigonal) sites and majority sites in the low-temperature phase.

In the low-temperature phase, the lattice distortion leads to two inequivalent Se sites.[3] The majority (75%) site coordination contains no rotational symmetry axis perpendicular to the layer and these sites should experience a nonaxial Knight shift. The minority (25%) sites retain trigonal symmetry although the principal axes are rotated and the interatomic distances change below T_0. The displacements leading to these two types of site are indicated in Fig. 4.

The axial resonance line of the minority site nuclei is evident only as an additional asymmetry in the low-temperature line shape (Fig. 1). The sharp peak of the axial resonance profile must nearly coincide with the central peak of the nonaxial majority resonance since only one main peak is observed. This implies that the value of $K_{\rm iso}$ for the minority sites may be somewhat larger than for the majority sites. In analyzing the line shapes below T_0, the presence of a minority-site resonance was disregarded and the values of $K_{\rm iso}$, $K_{\rm ax}$, $A_{\rm asym}$ represent shifts for the majority sites. This is a reasonably accurate procedure since the shift parameters were determined from the positions of the shoulders and main peaks of the line profiles and these are not strongly influenced by the presence of the weaker minority resonance. A detailed fit to superimposed axial and nonaxial resonances was not attempted.

Experimental values of the anisotropic Knight shift components $K_{\rm ax}$ and $K_{\rm asym}$ are plotted as functions of temperature in Fig. 5. The axial shift exhibits a weak temperature dependence and passes through a broad minimum near 200 K. The nonaxial component vanishes in the high-temperature phase but increases rapidly below T_0. The general shape of the temperature dependence of $K_{\rm asym}$ resembles that of an order parameter and is consistent with the second-order character of the phase transition as seen in the neutron diffraction data.[3] Extrapolation of the data to $K_{\rm asym} = 0$ yields a value $T_0 = 205 \pm 5$ K in agreement with the more precise value $T_0 = 201.5 \pm 5$ K determined from neutron diffraction.[3]

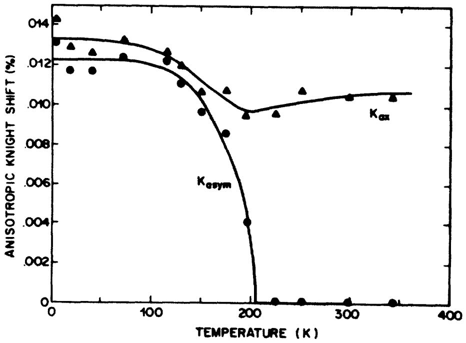

FIG. 5. Anisotropic Knight-shift components $K_{\rm ax}$ and $K_{\rm asym}$ vs temperature for ^{77}Se in $TiSe_2$.

B. Spin-lattice relaxation

Our results for the nuclear spin-lattice relaxation time T_1 are plotted in the form $(T_1T)^{-1}$ vs T in Fig. 6. It can be seen that $(T_1T)^{-1}$ is strongly dependent on temperature, decreasing first by a factor ~25 between room temperature and 77 K and then rising sharply to a maximum between 4.2 and 10 K.

We consider first the interpretation of the T_1 behavior for temperatures higher than about 40 K. Recalling that for s-electron contact interactions or p-electron core-polarization interactions one expects $T_1TK^2=\text{const}$,[18,19] we note the similarity of the tem-temperature dependences of $(T_1T)^{-1}$ and $K_{\rm iso}$ in this range. Furthermore, the data indicate that the dominant term in $(T_1T)^{-1}$ at room temperature has nearly vanished below 110 K, while $K_{\rm iso}$ retains a relatively large positive term whose corresponding relaxation process is very weak or nonexistent. These features of the data suggest the following decomposition of $(T_1T)^{-1}$ and $K_{\rm iso}$

$$(T_1T)^{-1}=(T_1T)_x^{-1}+(T_1T)_0^{-1} \ , \tag{4}$$

$$K_{\rm iso}=K_x+K_0 \ , \tag{5}$$

where $(T_1T)_x^{-1}$ and K_x are the temperature-dependent relaxation and shift terms, and $(T_1T)_0^{-1}$ and K_0 are assumed to be independent of temperature. The residual relaxation $(T_1T)_0^{-1}$ might be orbital or dipolar in origin and K_0 represents any temperature-independent terms in Eq. (3). Because of the qualitative similarity of the temperature dependences of $(T_1T)^{-1}$ and $K_{\rm iso}$ we assume a generalized Korringa relation

$$(T_1T)_x^{-1}=(1/S)K_x^2 \ . \tag{6}$$

In the absence of electron-electron effects, the theoretical value of $1/S$ for ^{77}Se is 1.39×10^{-7} (sec K)$^{-1}$ for s-electron contact interactions and $\frac{1}{3}$ this value for p-electron core-polarization interactions.[18,19]

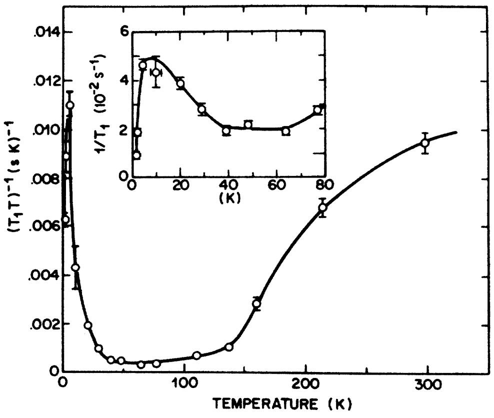

FIG. 6. ^{77}Se spin-lattice relaxation products $(T_1T)^{-1}$ vs temperature for TiSe$_2$. Inset shows relaxation rate $1/T_1$ in low-temperature range.

Equations (4)–(6) present no unique solution although, as following analysis shows, rather stringent limits can be placed on the physically allowed values of K_0, $(T_1T)_0^{-1}$, and $1/S$. Substitution of Eqs. (5) and (6) into (4) yields the expression

$$(T_1T)^{-1}=(1/S)(K_{\rm iso}-K_0)^2+(T_1T)_0^{-1} \ . \tag{7}$$

Now we can determine $1/S$ and $(T_1T)_0^{-1}$ for any choice of K_0 by plotting $(T_1T)^{-1}$ vs $(K_{\rm iso}-K_0)^2$. However, the requirement that $(T_1T)_0^{-1}$ be nonnegative places a lower limit $K_0\gtrsim0.075\%$; on the other hand, K_0 cannot exceed the minimum observed value of $K_{\rm iso}$ so we have $K_0\lesssim0.082\%$. Consequently, we find that K_0, $1/S$, and $(T_1T)_0^{-1}$ lie within the following ranges:

$$0.075\%\leq K_0\leq0.082\% \ ,$$

$$1.0\times10^{-7}\leq1/S\leq1.5\times10^{-7}\ (\text{sec K})^{-1} \ ,$$

$$0\leq(T_1T)_0^{-1}\leq5\times10^{-4}\ (\text{sec K})^{-1} \ .$$

The range of values for $1/S$ is particularly interesting since it encompasses the value $1/S=1.39\times10^{-7}$ (sec K)$^{-1}$ given by the normal Korringa relation for noninteracting s electrons. Inclusion of electron-electron effects may reduce this value by (30–40)% but such a reduced value would still lie within our inferred range. In contrast, the unenhanced Korringa constant for p electrons is 0.46×10^{-7} and is clearly incompatible with this analysis. The data strongly suggest, therefore, that the temperature dependences of $K_{\rm iso}$ and $(T_1T)^{-1}$ result from a small admixture of Se s character which is greatly reduced at the majority sites in the low-temperature phase.

The amount of s character present above T_0 can be roughly estimated from the magnitude of $K_{\rm iso}^{s}$. If we attribute K_0 to the sum $K_{\rm iso}^{\rm cp}+K_{\rm iso}^{\rm VV}-\sigma_{\rm chem}$, then the s electron contact shift at room temperature is just the difference between the experimental value and K_0, i.e., $K_{\rm iso}^{s}\simeq0.03\%$. Now Se in a metallic environment can be expected to have a Knight shift $K_{\rm iso}$ (metal) $=0.3\%$ for, say, two s electrons per Se. If we assume that the band edges are approximately free-electron-like (in three dimensions) we expect $K\propto\rho(E_F)\propto n^{1/3}$. This suggests an s-electron (or hole) concentration of about 10^{-3} per Se atom in TiSe$_2$ or roughly $\frac{1}{10}$ to $\frac{1}{3}$ the density of p holes estimated by DiSalvo *et al.*[3] from the dc transport properties.

The remaining relaxation in the range $40\lesssim T\lesssim100$ K is most likely of orbital and dipolar origin. A rough estimate of the orbital rate $(T_1T)_{\rm orb}^{-1}$ using Obata's expression[20] for p electrons gives $(T_1T)_{\rm orb}^{-1}\sim5\times10^{-4}$ (sec K)$^{-1}$, where we have taken $\langle1/r^3\rangle\simeq1\times10^{24}$ cm^{-3} and $\rho_p(E_F)\sim1\times10^{11}$ (erg atom)$^{-1}$ for the orbital hyperfine coupling and density of states, respectively. The density of states corresponds to the values of carrier concentration and Fermi energy obtained by DiSalvo *et al.*[3] This value of $(T_1T)^{-1}_{\mathrm{orb}}$ as well as the dipolar term, smaller by a factor $\frac{3}{10}$, is of the right order of magnitude to explain the residual relaxation.

The residual relaxation may also be used to place an upper limit on the magnitude $|K^{\mathrm{cp}}_{\mathrm{iso}}|$ of the *p*-electron core-polarization component of the shift. We use the appropriate Korringa relation

$$(T_1T)^{-1}_{\mathrm{cp}} = (0.46\times10^{-7})(K^{\mathrm{cp}}_{\mathrm{iso}})^2 \quad .$$

Since, in the range $40 \lesssim T \lesssim 100$ K, $(T_1T)^{-1}_{\mathrm{cp}} \lesssim (T_1T)^{-1}_{\mathrm{expt}} \simeq 5\times10^{-4}$ $(\sec\mathrm{K})^{-1}$, we have $|K^{\mathrm{cp}}_{\mathrm{iso}}| \lesssim 0.01\%$. Therefore, the dominant-shift contributions in this range must be the orbital $(K^{\mathrm{VV}}_{\mathrm{iso}})$ and chemical shift $(-\sigma_{\mathrm{chem}})$. At higher temperatures, where $(T_1T)^{-1}$ is much larger, there could be a larger contribution from $K^{\mathrm{cp}}_{\mathrm{iso}}$ but, as we have already noted, the experimental value of $1/S$ is too large to allow $K^{\mathrm{cp}}_{\mathrm{iso}}$ and $(T_1T)^{-1}_{\mathrm{cp}}$ to be dominant.

Finally, we comment on the peak in $(T_1T)^{-1}$ observed at low temperatures. This effect is particularly interesting because there is virtually no change of corresponding magnitude in the value of the Knight shift. The low-temperature variation of $(T_1T)^{-1}$ is therefore of a clearly different origin than the behavior above 100 K where $(T_1T)^{-1}$ and K_{iso} exhibit related temperature dependences. It is unlikely that the effect is due to paramagnetic impurities or to heating of the sample by the rf pulses since neither of these should lead to a peak in the relaxation rate $1/T_1$ (Fig. 6).

There is little independent evidence for a change in the electronic or magnetic properties below 40 K. The conductivity and Hall coefficient exhibit no anomalous behavior and are nearly independent of temperature in this range.[3] The thermopower, negative at low temperatures, does show a rise toward less-negative values on cooling below 40 K.[3] However, it is unclear whether this is related to the $(T_1T)^{-1}$ anomaly since the thermopower behavior may be a normal phonon-drag effect. The bulk magnetic susceptibility is dominated by a Curie-like tail which was attributed to the presence of paramagnetic impurities in low concentrations.[3] For this reason interpretation of the susceptibility is ambiguous at low temperatures.

The peak in $(T_1T)^{-1}$ is suggestive of relaxation behavior observed in weak itinerant ferromagnets and and antiferromagnets, i.e., those with low-transition temperature and magnetization much less than $1\mu_B$ per atom.[21-23] Normally the onset of magnetic order leads to a significant shift of the resonant frequency as well as to anomalies in the transport properties. In the case of weak antiferromagnetism, however, it is possible to obtain divergent behavior in the staggered susceptibility and nuclear relaxation rates while the uniform susceptibility and Knight shift preserve weak temperature dependences. Such behavior has been observed in β-Mn alloys although even in that case broadening of the NMR was observed in the vicinity of the Néel temperature.[21] In contrast, the resonance was observed to vanish at the transition temperature of the weak antiferromagnet $\mathrm{CrB_2}$.[23] For $\mathrm{TiSe_2}$ we have no evidence of magnetic ordering other than the peak in relaxation rate and it must remain an open question whether such a transition is present. As an alternative to magnetic ordering, for example, it is possible that the relaxation reflects some additional structural transition or is related to the motions of atoms in the Van der Waals gap.

IV. SUMMARY AND CONCLUSIONS

A principal result of this investigation is the conclusion that the electronic states at the Fermi level in $\mathrm{TiSe_2}$ contain some (10–30)% Se *s* character in the high-temperature phase, and that this *s* character is greatly reduced well below T_0. This observation, in conjunction with transport data showing a lower carrier density below T_0,[3] indicates that the electrons removed from the Fermi surface have strong *s* character at the Se sites. The residual shift and relaxation rate below T_0 are due primarily to *p*-electron orbital and dipolar effects.

In the low-temperature phase the temperature dependence of K_{asym} for the majority sites is similar to that of the order parameter for the second-order phase transition.[3] The axial shift, in contrast, is only weakly affected by the transition. It was not possible to resolve the resonance of the minority trigonal sites whose main effect is the introduction of additional asymmetry in the line shape.

We have observed only weak evidence of an additional transition in the range where extra spots have been observed in electron diffraction (110–140 K). A slight change of slope in the temperature dependence of K_{iso} near 130 K is the only hint of an effect in the NMR data and even this feature must be viewed with caution since it lies just at the limit of experimental resolution. There is no indication that this effect is related to an incommensurate charge-density wave which could be expected to alter the line shape significantly due to a distribution of Knight shifts.

Finally, a peak in the nuclear relaxation rate at low temperatures is suggestive of weak antiferromagnetism. However, the absence of any effect in the line shape, Knight shift, and electrical resistivity is puzzling and it is by no means certain that magnetic ordering is the correct explanation of this effect. The possible role of further structural changes and interlayer atoms needs to be investigated in this connection.

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