Amplitude of the Charge-Density Waves in $1T$- and $2H$-TaSe$_2$

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Mössbauer ^{181}Ta spectra of $1T$-TaSe$_2$ at 300 K show only two of three Ta sites predicted by 6:6:1 charge-density-wave models. They have equal amplitude and are separated by a shift the authors calibrate as 0.34(0.17) electrons. The unseen site is experimentally excluded from the region between Ta^{4+} and Ta^{5+}. Site linewidths limit possible secondary splittings by interlayer effects to 0.018 of the primary splitting. The $2H$-TaSe$_2$ data at 52 K are consistent with an orthorhombic charge-density wave with three equal Ta sites at $-0.049(0.020)$, $+0.033(0.016)$, and $+0.023(0.011)$ electrons relative to Ta^{4+}.

The $2H$ and $1T$ polytypes of the layered compound TaSe$_2$ have received much attention as two-dimensional metals that exhibit striking charge-density-wave (CDW) superlattice effects. In both materials the CDW arises in the Ta $5d$ conduction bands. The $2H$ polytype exhibits a rich diversity of CDW superlattice phenomena including transitions[1,2] between fully commensurate, striped discommensurate, and honeycomb discommensurate states. In the $1T$ polytype the interactions responsible for the CDW are several times stronger so that only a large-amplitude, fully commensurate CDW is observed[3] near room temperature and below.

CDW's in these materials have been studied for the most part by neutron,[4] x ray,[5] and electron diffraction,[1,2] which are sensitive to the small periodic distortions in the Ta and Se lattice positions induced by the CDW. A complementary approach is to look directly for the presumed variations of Ta $5d$ conduction-electron density, through their effects on Ta or Se probe atoms monitored in nuclear-magnetic resonance (NMR), perturbed angular correlation (PAC), x-ray photoelectron spectroscopy (XPS), or Mössbauer experiments. Results on CDW's in TaSe$_2$ by PAC[6] on ^{181}Ta and by NMR on ^{77}Se[7] and ^{181}Ta[8] have been reported and have been useful, but are so far uncalibrated in terms of CDW variations in the Ta $5d$ electron amplitude. XPS splittings on the $4f$ levels of Ta in the $1T$ material have been reported by two groups,[9,10] but there is disagreement between them by more than an order of magnitude in the proposed CDW amplitude.

We report here ^{181}Ta Mössbauer isomer-shift spectra for the CDW's in both polytypes, and suggest a method for calibration of our results. This allows us to measure the CDW amplitude directly in terms of the number of Ta $5d$ electrons. The ^{181}Ta Mössbauer effect is especially appropriate for this application, because of all

the Mössbauer isotopes ^{181}Ta has the highest sensitivity to small changes in the electron density at the nucleus. This is the first such measurement for $2H$-TaSe$_2$. Our results[11] for $1T$-TaSe$_2$ disagree with recent synchrotron-XPS estimates by Pollack *et al.*,[10] but are in approximate agreement with the early XPS estimate of Wertheim, Di Salvo, and Chiang.[9]

The ^{181}Ta Mössbauer data were obtained in transmission geometry with a γ-ray proportional counter and a conventional electromechanical drive. The ^{181}W source activity was diffused into tungsten. The absorbers were a mosaic of 2×3-mm^2 single-crystal platelets 5 μm thick with the plane of the layers normal to the γ rays. Where required the TaSe$_2$ absorber was cooled by a closed-cycle He refrigerator with a vibration-isolation Mössbauer shroud.[12]

Each layer of TaSe$_2$ consists of a plane of Ta atoms sandwiched between a pair of Se atomic planes. Each Ta atom has six Se near neighbors that are arranged in trigonal prismatic coordination in the $2H$ polytype, and in octahedral coordination in the $1T$ polytype. Figure 1 shows the ^{181}Ta Mössbauer spectra of both polytypes at room temperature. The $2H$ material, which has no CDW at this temperature, shows a single Ta site that is split into several resonance lines by the electric quadrupole hyperfine interaction.[13] The solid curve is a data fit using the parameters given in the caption. The arrow marks the isomer shift of the site. The linewidths of this spectrum and the others reported here are dominated by velocity broadening arising from the small source-absorber spacing required by source strength considerations.

Electron[3] and x-ray diffraction[5] show that the atomic positions are distorted by the CDW in $1T$-TaSe$_2$ to form a triclinic superlattice containing thirteen Ta atoms per layer in three sites of population 6:6:1 with $a = b = 13^{1/2}a_0$, where a_0 is
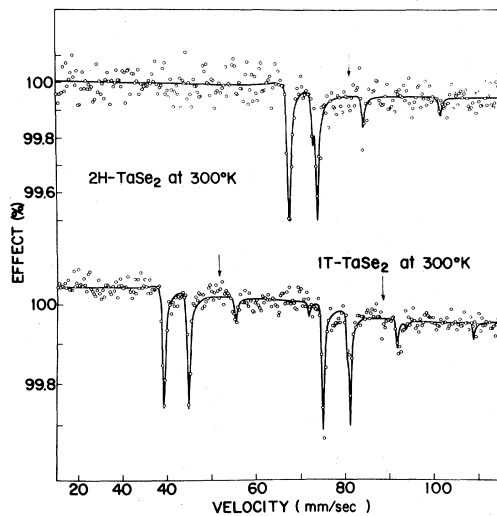
FIG. 1. Mössbauer ^{181}Ta spectra at 300 K. (Parameters in millimeters per second.) $2H$: linewidth $=0.7(0.1)$, shift$=+81.9(0.1)$, $e^2qQ=243(1)$; $1T$ inner: width$=0.6(0.1)$, shift$=+52.7(1)$, $e^2qQ=230(1)$; $1T$ outer: width$=0.7(0.1)$, shift$=+89.1(1)$, $e^2qQ=239(1)$.

the undistorted Ta-Ta separation. The $1T$ ^{181}Ta Mössbauer spectrum of Fig. 1 shows just two hyperfine-split Ta sites. A fit to the data locates their isomer shifts at the arrows which are separated by 36.4(2) mm/sec. No third Ta site was found within the range −165 to +165 mm/sec, but its presence might be obscured at this level of statistical noise. The resonance areas of the sites are equal to within the statistical error, $A_{inner}/A_{outer}=0.98(0.10)$. This disagrees with the XPS measurements of Pollack et al.[10] who also found two sites but with $A_{smaller}/A_{larger} = 0.70(0.04)$. They concluded that their data are irreconcilable with three Ta sites having 6:6:1 intensity ratio. The ratio of the individual Mössbauer widths to the separation between sites is 0.018. For the XPS data this ratio is 0.34. An accidental site overlap is possible, especially in the XPS data. This would tend to resolve the disagreement between the experiments. On the other hand Mössbauer is a bulk measurement and XPS is sensitive only to Ta atoms within 20 Å of the sample surface. From this point of view the disagreement could be evidence of changes in the CDW near the sample surface.

Our observation of two equally populated sites and the strong x-ray evidence[5] for the 6:6:1 model leads us to identify the sites in Fig. 1 with the two six-atom sites of that model. Each Mössbauer site is thus a composite arising from six very similar Ta atoms in the CDW superlattice.

TABLE I. Isomer shifts of ^{181}Ta compounds referred to Ta metal at zero.

		Isomer shift	Ta coordination	Bond length
Ta^{4+}	TaSe$_2$(2H) [a]	82.7 mm/sec	6 − Se	2.60 Å
	TaS$_2$(2H) [a]	70.3	6 − S	2.46
	TaC [b]	70.8	6 − C	2.23
Ta^{5+}	Cu$_3$TaSe$_4$ [c]	32.6	4 − Se	2.31
	Cu$_3$TaS$_4$ [d]	15.2	4 − S	2.26
	K TaO$_3$ [b]	− 8.1	6 − O	1.99
	NaTaO$_3$ [e]	− 15.4	6 − O	1.94
	LiTaO$_3$ [e]	− 17.9	6 − O	2.11

[a]Ref. 15.   [d]Ref. 17.
[b]Ref. 13.   [e]Ref. 18.
[c]Ref. 16.

The 0.018 resonance linewidth then puts an 0.018 upper limit on overlap smearing of either site by interlayer interactions or deviations of the center of symmetry of the CDW away from a Ta atom. This low limit on interlayer effects is noteworthy, because large distortions of the ^{77}Se NMR site positions have been seen and attributed to interlayer effects in this material.[14]

A computer search of all possible CDW's of the form $\rho_0\sum_{i=1}^{3}\cos(\vec{G}_i\cdot\vec{r}_j+\varphi_i)$ at the thirteen Ta sites $\vec{r}_j$, allowing the phase angles φ_i to vary independently over 0 to 2π, shows that the only solution with three or fewer inequivalent Ta sites is the known 6:6:1 solution for which the CDW origin is at a Ta atom. For CDW's without harmonic terms our 0.018 limit on overlap smearing requires that φ_1, φ_2, and φ_3 each be within 1.2° of zero at the CDW origin.

The 36.4-mm/sec shift in Fig. 1 is direct evidence that the Ta valence varies from place to place in the $1T$ superlattice. We now discuss a calibration of the shift that allows us to specify its amplitude. Table I lists all chemical compounds for which a ^{181}Ta Mössbauer shift has been reported, with the shift, formal Ta oxidation state, Ta coordination, and bond length. We note that there is a general, but not detailed, correspondence between the formal Ta valence and the shift. A proper calibration would require shifts between pairs of compounds with different Ta oxidation states, but with equivalent neighboring atoms, and coordination. As this is not now possible we use a semiquantitative electronegativity argument to account for the shift associated with substitution of Se for S in pairs of otherwise similar compounds.

Consider first the pair $2H$-TaS$_2$ and $2H$-TaSe$_2$. Each chalcogen atom is shared by three Ta atoms, and every Ta is bonded to six of these $\frac{1}{3}$-value chalcogens. The result is equivalent to two bonds containing four bonding electrons as expected from the stoichiometry. The S-Ta electronegativity[19] difference is 2.5−1.5 = 1.0 which following Pauling[20] corresponds to 22% ionicity. For the Se-Ta bonds this difference is 2.4−1.5 = 0.9 or 19% ionicity. Thus substitution of Se for S increases the covalency by about 0.12 electron for the four bonding electrons taken together. If because of their other similarities we attribute the +12.4-mm/sec shift difference in Table I to this effect, we see by scaling that adding one covalent electron would correspond to a shift of +103 mm/sec. For the Ta^{5+} compounds Cu$_3$TaS$_4$ and Cu$_3$TaSe$_4$ the argument suggests a 3% covalency increase for each of the five Ta-chalcogen net bonding electrons allowed by the stoichiometry, or an additional 0.15 electron in going from the sulfide to the selenide. Scaling this with the +17.4-mm/sec shift difference of Table I gives a second calibration, this time equal to +116 mm/sec for the additional covalent electron.

A third and independent Ta calibration is also possible. Here we use the empirical ratio of isomer-shift differences for ^{181}Ta and ^{57}Fe in pairs of host metals. These data obtained from Mössbauer source experiments using many host pairs were tabulated by Kaindl, Salomon, and Wortmann[13] and give the result $\Delta S(^{181}\text{Ta})/\Delta S(^{57}\text{Fe})$ =218. Noting this and that the isomer shift corresponding to one electron near Fe^{4+} is 0.45 mm/sec results in a Ta calibration near Ta^{4+} of 98 mm/sec for a one-electron change.

In view of the semiquantitative nature of these arguments their agreement is quite close. We will adopt a simple average of the three, giving 106 mm/sec which we estimate calibrates the
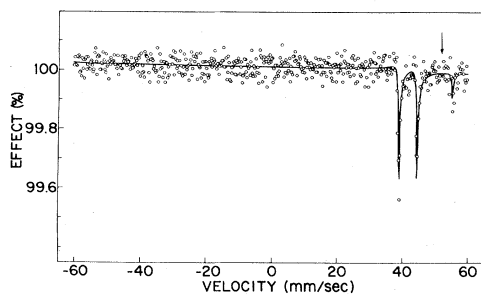
^{181}Ta isomer shift between Ta^{4+} and Ta^{5+} to well within 50% including possible errors associated with applicability of the electronegativity concept. Thus the $1T$-TaSe$_2$ CDW splits the two sites in Fig. 1 by 0.34(0.17) electron.

Figure 2 reports a search for the missing third site of the 6:6:1 trio in the neighborhood of Ta^{5+}. The signature of this site would be a pair of hyperfine resonances of at least 0.06% amplitude spaced between 4 and 8 mm/sec apart. The data of Fig. 2 are adequate to exclude the missing site from the region scanned. This implies that the unseen site must be located on the Ta^{3+} side of the main site pair. The sign of the $1T$-TaSe$_2$ CDW thus reflects a clustering of conduction electrons around every thirteenth Ta atom. This picture is consistent with the model of star-shaped clusters of Ta ions that was proposed by Brouwer and Jellinek[5] to explain their x-ray data. Clusters of positive Ta ions and negative $5d$ conduction electrons overlap in phase so as to preserve local charge neutrality in the solid.

Our calibration is also useful for measuring the CDW amplitude corresponding to the well-known nine-Ta-atom superlattice that forms below 120 K in $2H$-TaSe$_2$. Mössbauer spectra of this material are shown in Fig. 3. Extrapolation of the isomer shifts (vertical arrows) of the single-site spectra at 300 and 130 K locates the expected shift center of the 52-K spectrum, which
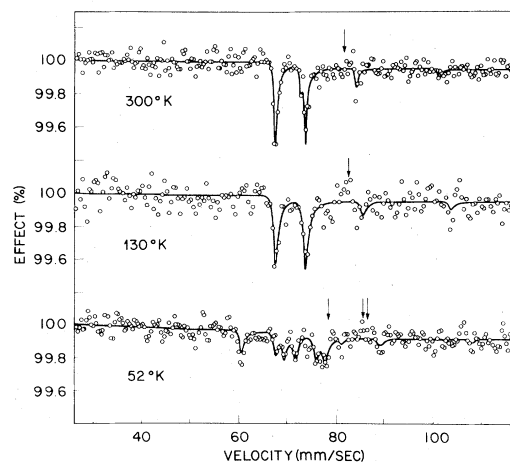

FIG. 3. Mössbauer ^{181}Ta spectra of $2H$-TaSe$_2$ at three temperatures. (Parameters in millimeters per second.) 300-K spectrum: linewidth = 0.6(0.1), shift = 81.9(0.1), e^2qQ = 243(1); 130-K spectrum: linewidth = 1.2(0.1), shift = 83.0(0.2), e^2qQ = 255(1); 52-K spectrum: linewidth = 0.8(0.1), shift 1 = 78.3(0.3), shift 2 = 87.0(0.3), shift 3 = 85.9(0.3), $e^2qQ(1)$ = 293(7), $e^2qQ(2)$ = 253(7), $e^2qQ(3)$ = 273(7).

FIG. 2. Mössbauer ^{181}Ta spectrum of the inner site of $1T$-TaSe$_2$ at 300 K.

is split into several inequivalent sites by the fully commensurate CDW that forms below 90 K.

The statistical quality of the 52-K spectrum is adequate to distinguish between the 3:3:3 Ta-site model with orthorhombic CDW symmetry[21] and the 6:2:1 Ta-site model required of a CDW with hexagonal symmetry.[21] The curve is a fit to the 52-K data under the assumption of the 3:3:3 orthorhombic model with the usual hyperfine splittings. Using the calibration and the locations of the pattern center discussed above allows us to specify these sites as −0.049, +0.033, and +0.023 electron with a precision of 15% and an accuracy of 50%. A preliminary and uncalibrated version of these Mössbauer data was communicated to Walker and Jacobs in July 1981. This, together with the important convergent-electron diffraction work of Fung $et\,al.$,[1] was used by them shortly afterward[22] to justify introduction of their now accepted model[21] of orthorhombic symmetry in the fully commensurate CDW phase of $2H$-TaSe$_2$.

We thank A. P. Ginsberg, G. K. Wertheim, P. B. Littlewood, and M. B. Walker for helpful discussions. We also thank D. Salomon for preparing the ^{181}W Mössbauer sources used in obtaining the data of Fig. 1.

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