Direct determination of Debye temperature and electron-phonon interaction in $1T$-VSe_2

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(Received 2 October 2000; published 30 January 2001)

Crystals of the layered two-dimensional transition-metal dichalcogenide $1T$-VSe_2 are investigated by point-contact spectroscopy in the charge-density wave state. Relevant characteristics such as mean, root-mean-square, and Debye phonon frequencies are obtained. The Debye temperature is $\Theta_D = 220 \pm 5$ K, close to that of $2H$-$NbSe_2$. The point-contact function $g_{pc}(\omega)$ of the electron-phonon interaction reveals a moderate coupling constant $\lambda_{pc} = 0.27$. Consequently, the Coulomb potential, the density of states at the Fermi level, and the deformation potential are estimated to be of order 0.22 eV, 2.5 states/eV, and 0.22 eV/Å, respectively.

DOI: 10.1103/PhysRevB.63.073107 PACS number(s): 71.45.Lr, 63.20.Kr, 63.22.+m, 85.30.Hi

$1T$-VSe_2 belongs to quasi-two-dimensional layered dichalcogenides which are known to display remarkable properties like condensation of conduction electrons in charge-density or spin-density waves (CDW, SDW). $1T$-VSe_2 is a paramagnetic metal, in which vanadium atoms are situated in an octahedral environment of a trigonally distorted cage of selenium atoms.[1,2] The sandwiched structure of $1T$-VSe_2 presents strong covalent bonding inside each layer and weak van der Waals forces between them. This results in a narrower conduction band (0.3 eV) with respect to other dichalcogenides (>1 eV) and in an increased Coulomb repulsion reducing CDW formation. The small overlap of electron wave functions inside the metallic layers is at the origin of both quasi-two-dimensionality and high anisotropy of physical properties in this system. In the CDW phase, this material has a commensurate $4\mathbf{a}_0 \times 4\mathbf{a}_0$ superstructure in the layers and is incommensurate perpendicularly to them with a component of $\approx 3\mathbf{c}_0$.[3] The CDW onset and lock-in transition temperatures occur at $T_0 = 112$ K and $T_l = 62$ K, respectively. The CDW gap Δ opens up near 40 meV at 4.2 K.[4]

Although $1T$-VSe_2 is among compounds which have been investigated quite intensively in the past, vital informations about quasiparticle spectra in this material are still missing. It appears that such data cannot be circumvented since in fact, despite electronic band structure and Fermi surface were quite well determined[5–10] at the same time the phonon subsystem and its properties were insufficiently documented. For instance, we could not find any literature data about phonon dispersion curves, phonon density of states (PDOS), electron-phonon interaction (EPI), Debye temperature, specific heat, sound velocity, etc., which appear to be most essential to pinpoint the electrophysical properties of this model compound. In principle this lack of information is not surprising since lamellar dichalcogenides are not easy to study by traditional methods able to yield the above characteristics. Since the susceptibility at low temperature in $1T$-VSe_2 exhibits a Curie tail, magnetic interactions dominate and preclude the determination of specific heat and EPI parameter.[11] Additionally, optical measurements of this compound show weak signal-to-noise ratios due to high reflectivity and metallic behavior in the CDW state. In particular, the Raman modes are more or less smeared out and weaker than those of $2H$-$TaSe_2$ by at least one order of magnitude.[12] Therefore, in this paper, we focus primarily at investigating the phonon subsystem in $1T$-VSe_2 and the interaction of quasiparticle excitations with current carriers. This will allow for the determination of the EPI function in the CDW state and other quantities.

Point-contact spectroscopy (PCS) was found to be a particularly suitable technique to achieve this task since its prospects overcome greatly those provided by other methods for similar investigations. PCS experiments were conducted on heterocontacts $1T$-VSe_2/Cu using the original point-contact spectrometer developed at the B. Verkin Institute for Low Temperature Physics of Kharkov (ILT). Contacts on $1T$-VSe_2 were set up by means of devices and methods which proved to be very successful in investigating organic conductors with similar layered structure.[13] We have chosen the displacement technique[14] in which contacts are created between a copper prism electrode and the edge face of lamellar freshly clived $1T$-VSe_2 crystals. This method was found to provide reliable contacts within an axis preferably oriented parallel to the layers of the structure. Such contacts allowed to deliver the crystal properties in the current flowing regime along the sandwiched layers. Raman spectra excited at the $\hbar\omega_L = 2.41$ eV line of an Ar^+ laser were collected under a microscope (objective $\times 50$) with a triple monochromator equipped with a liquid-nitrogen cooled charge-coupled device detector. The laser power density was ≈ 0.2 MW/cm^2. PCS experiments were made in a helium cooled cryostat operating in the 1.5–100 K range. Point contact characteristics were carried out at 4.2 K.

The voltage-current characteristic (IVC) of contacts is the main source of spectroscopic information in PCS investiga-

tions. The IVC contains nonlinearities resulting from current carrier scattering on phonons and other quasiparticle excitations when the current flows through the contact.[15] After derivation, these nonlinearities transform into the IVC second derivative

$$V_2 \propto \frac{d^2I}{dV^2} \tag{1}$$

whose maxima correspond to PDOS singularities. In turn, the knowledge of the IVC second derivative spectra allows the determination of the EPI function $g_{\mathrm{pc}}(\hbar\omega)$ of the materials under study according to the equation

$$\frac{d^2I}{dV^2}(V) = \frac{-\pi e^3}{\hbar\langle K\rangle}\Omega_{\mathrm{eff}}N(E_F) \times \int_{-\infty}^{\infty} d(\hbar\omega)g_{pc}(\hbar\omega)\otimes\chi(z), \tag{2}$$

where K is the form factor (see below), Ω_{eff} the effective volume of phonon generation, $z=(\hbar\omega-eV)/kT$ and $\chi(z)$ the temperature broadening function.

In this work, IVC and second derivative acquisitions were performed for a voltage range of 0–120 mV. At higher bias instability of electrical resistance or even complete destruction of contacts took place. Probably they were caused by heating effects around the contact area.

More than 50 contacts were investigated, and 32 of them yielded good quality spectra corresponding to the spectral current regimes. PCS spectra with clearly expressed features, which were well reproducible in the IVC second derivatives for different contacts, were observed when realizing ballistic and diffusive current flowing regimes. Two typical IVC second derivatives well representative of the highest intensity EPI spectra are shown in Fig. 1 [curves (a) and (b)].

Concerning the present experiments, we shall mention that the PCS spectrum of a heterocontact is normally the sum of each spectral contribution arising from contact electrode materials.[16] However, in the case of $1T$-VSe_2/Cu heterocontacts no copper contribution in PCS was seen. Such a result is in qualitative agreement with data obtained for $2H$-$NbSe_2$/Cu contacts[17] and for Nb, Ta heterocontacts[18,19] which are electronic analogs of vanadium in the VB group.

The IVC second derivatives of $1T$-VSe_2 are presented in Fig. 1, curves (a) and (b). They display wide EPI spectra bounded at $\omega_{\max}=88$–90 meV. This result can be qualitatively compared with PCS measurements in pure vanadium.[15,20] According to Ref. 15 the highest frequency phonons in PCS of vanadium correspond to an energy of about $\omega_{\max}=60$ meV. Thus, comparatively, $\omega_{\max}$ is largely increased in VSe_2. Taking into consideration that the EPI spectral boundary in the analogous $NbSe_2$ compound is shifted to the high-energy side by approximately 30 meV when moving from pure niobium to $NbSe_2$[15,19] the $\omega_{\max}$ value determined for $1T$-VSe_2 seems quite reasonable.[15,19]

The strongest line in the PCS spectra of $1T$-VSe_2 is located in the low-frequency range at an energy of 5–7 meV and weaker features are observed at 25 and 40 meV. These positions coincide with the Raman lines observed by us and

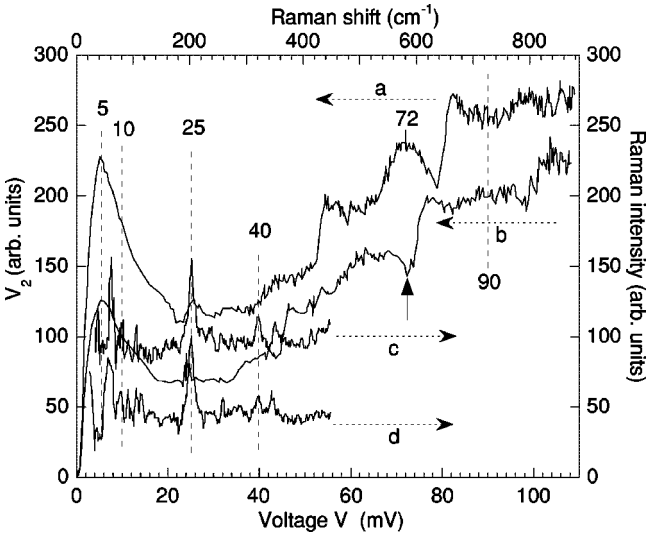

FIG. 1. Vibrational spectra of $1T$-VSe_2. IVC second derivatives of $1T$-VSe_2/Cu contacts, $R_0=84\Omega$ [curve (a)], 78Ω [curve (b)], $T=4.2$ K; Raman spectra at $T=180$ K [curve (c)] and $T=10$ K [curve (d)].

by other authors.[12,19] In addition, the intensity of the low-energy PCS peaks is considerably enhanced. This can be explained by a decrease of the relative intensity of the high-frequency peaks consecutive to the influence of the point-contact form factor K. This form factor depends on the geometry and the purity of the contact. It favors large angle scattering and increases Umklapp processes at backward electron scattering. These effects are especially well displayed in metals with complicated Fermi surface.[21,22] Therefore, in comparison with optical experiments, high-energy features in PCS of $1T$-VSe_2 have essentially weaker relative intensity than low-frequency ones [see, for example, the maxima at 48 cm^{-1} and 203 cm^{-1} in curves (c) and (d) of Fig. 1, in Ref. 12, and corresponding peculiarities in PCS spectra].

Considering literature data on conducting properties of $1T$-VSe_2 from the PCS point of view, a current regime characterized by a destruction of the electron states localization can be realized in the contacts of this compound, as observed for semimetal contacts. This regime was investigated earlier in Sb[23] and organic conductors.[13] Electroconductivity parameters play a prominent role in this process. For instance, the resistivity of $1T$-VSe_2 is about 10^{-4} Ω cm at $T=20$ K,[24] i.e., lesser by two orders of magnitude than that in Sb.[25] In $1T$-VSe_2 contacts, the EPI destroys electron localization for small elastic electronic mean free paths near the contact area thus leading to a development of contact conductivity. In such a situation, inverse PCS spectra will emerge.[26] An accumulation of phonons in the constriction area upon bias increase is likely to be at the origin of the electron mean-free path decrease. In this case the electron flowing regime through the contact changes from a ballistic to a diffusive behavior when weak localization effects prevail. As a consequence PCS spectra of intermediate type should disclose inverse peculiarities at high voltage. An example of such a

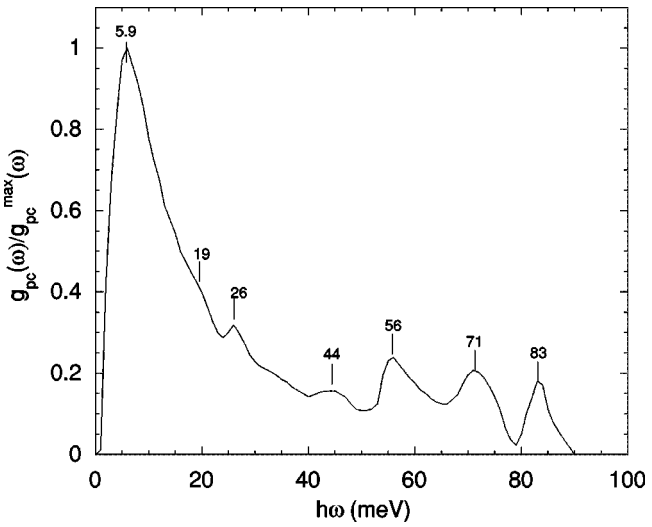

FIG. 2. Point-contact EPI function $g_{pc}(\omega)$ reconstructed from curve (a) in Fig. 1.

characteristic is given by curve (b) (Fig. 1), in which maxima and minima are mirror reflections of corresponding ones in curve (a) above a bias of 60 mV.

PCS of $1T$-VSe_2/Cu heterocontacts was used to calculate the point-contact EPI function $g_{pc}(\omega)$ which can be expressed as

$$g_{pc}(\omega)=\frac{(2\pi\hbar)^{-3}}{\oint_{FS}\frac{dS}{v}}\langle K\rangle_{FS}^{-1}\oint_{FS}\frac{dS\,dS'}{vv'}\times\sum_{s}|M_{\mathbf{p}-\mathbf{p}',s}|^2\times K(v,v')\,\delta(\omega-\omega_{\mathbf{p}-\mathbf{p}',s}), \tag{3}$$

where $\mathbf{p},\mathbf{p}'$ and v,v' are electron quasimomentum and velocity, $|M_{\mathbf{p}-\mathbf{p}',s}|$ is the EPI matrix element modulus for the $\mathbf{p}\rightarrow\mathbf{p}'$ transition summed over all branches of the phonon spectrum, accounting for the scattering process of a phonon with momentum $\mathbf{q}$ $(\mathbf{p}'=\mathbf{p}-\mathbf{q}+\mathbf{Q})$. dS and dS' are the elements of Fermi surface for electrons before and after scattering. The Eliashberg function $g_{pc}(\omega)$ is represented by the product of the PDOS $F(\omega)$ with the Fermi surface average of the electron-phonon interaction $\alpha^2(\omega)$. In the case of clean circular aperture contacts, $K=\frac{1}{8}(1-\theta/\tan\theta)$, where θ is the scattering angle. This means that large angle scattering contributes predominantly to g_{pc}. Thus, backward scattering processes ($\theta\approx\pi$) are essential in point contacts.

The plot of $g_{pc}(\omega)$ obtained for dependence (a) in Fig. 1 is shown in Fig. 2. The calculation was made by means of a software package[27] in which a point-contact background linear function was used.[15] The EPI dimensionless parameter λ_{pc} is given by

$$\lambda_{pc}=2\int_0^\infty g_{pc}(\omega)\omega^{-1}\,d\omega. \tag{4}$$

The value obtained for curve (a) is $\lambda_{pc}=0.27$ which is much lesser than in pure vanadium (0.83), organic superconductors (0.4 to 0.9),[28,29] and $NbSe_2$ (0.89).[30] This value should be considered close to the upper limit since it is difficult to uphold that the current regime in the present heterocontacts is ballistic. We find that the values of mean $\langle\omega\rangle$ and root-mean-square $\langle\omega^2\rangle^{1/2}$ phonon frequencies are 10.14 and 16 meV, respectively for curve (b). The Debye phonon frequency and Debye temperature Θ_D can be deduced from the relationships[31]

$$\omega_D=\left(\frac{3}{2}\langle\omega^2\rangle\right)^{1/2},\quad \Theta_D=\frac{\hbar\omega_D}{k_B}. \tag{5}$$

Average values for 5 PCS spectra are $\Theta_D=220\pm5$ K and $\omega_D=153\pm4$ cm^{-1}. As a rule, it should be noted that the Θ_D values derived from PCS are a little lower than those obtained from temperature measurements of electronic heat capacity in Pt, Pd, Rh, Ir, and Os.[32] Again, this has to be explained by the influence of the point-contact form factor. As a result, the high frequency spectral features of the point-contact EPI function $g_{pc}(\omega)$ decrease in intensity with respect to those of the PDOS function. However, we get the same Θ_D than in $2H$-$NbSe_2$ (220 K).[33–35]

We can discuss shortly the relation between the EPI and the CDW state in $1T$-VSe_2 as follows. The CDW state is normally caused by strong electron-phonon coupling and bears some analogy with the superconducting state. In superconductivity, due to the nature of the phonon-mediated interaction, the attractive forces between electrons are exerted only if their energy lie in a narrow interval of $\approx\hbar\omega_D(\hbar\omega_{max})$. At other energies the electrons also interact by means of phonon exchange but they repel one another. This fact leads to the BCS prefactor $\hbar\omega_{max}$ and correspondingly to the isotopic effect on T_c. Quite different is the situation with CDW. In this case, there is also electronic scattering. However, single electrons interact via the static lattice distortion, created by the EPI, which accompanies the CDW. Therefore, there is no restriction on the energy of the electrons which may lie well below E_F. Accordingly, the BCS-type equation in the CDW state should read

$$k_BT_0\approx E_F\exp(-1/\lambda_{pc}) \tag{6}$$

with $E_F\approx1/N(E_F)$. In $1T$-VSe_2 the moderate value of λ_{pc} seems to result in a stronger competition between the EPI and the Coulomb repulsion U as expected from the band structure. According to the Chan–Heine criterion[35,36]

$$\frac{4\lambda_{pc}}{N(E_F)}\geqslant2U \tag{7}$$

this suggests that CDW stabilization in $1T$-VSe_2 occurs if $U\leqslant0.22$ eV, a limit close to the experimental d bandwidth. Within this approach, it can be noticed that the one-spin density of states at the Fermi level is of the same order as that of $2H$-$NbSe_2$ (2.2 states/eV Nb atom)[30] since $N(E_F)=2\lambda_{pc}/U\approx2.5$ states/eV V atom. Furthermore, if V is the EPI matrix element averaged over the first Brillouin zone one has

$$\lambda_{pc}=\frac{2N(E_F)V^2}{\langle\omega^2\rangle^{1/2}}. \quad (8)$$

We find $V=29$ meV. The quantity V is of the same order of magnitude as that of the modulation of the electronic state energy δE which is produced by the atomic displacement δx during the vibration

$$\delta x\approx\langle x^2\rangle^{1/2}=\left(\frac{\hbar}{2M\langle\omega^2\rangle^{1/2}}\right)^{1/2}, \quad (9)$$

where M is the vanadium atomic mass. Thus, the deformation potential can be defined as $V_D=\delta E/\delta x$, which yields $V_D\approx V/\delta x$. We obtain $\delta x=0.13$ Å, and finally $V_D=0.22$ eV/Å.

In summary, a weak-coupling electron-phonon interaction in the CDW state of the metal-rich $1T$-VSe_2 model compound has been directly determined via the PCS technique. The good reproducibility of the results provides for the estimation of the Debye phonon spectrum, and CDW physical parameters which were unknown before. With respect to $NbSe_2$ ($T_c\approx 7$ K), the dimensionless λ parameter of coupling obtained at 4.2 K is small, but the density of states at the Fermi level and the Debye temperature are of the same order of magnitude.

The authors acknowledge Dr. A. V. Yeremenko and Dr. A. R. Kazachkov for useful discussions, and Dr. V. V. Khotkevich for assistance in EPI function calculations. This work was supported by the NATO Grant No. CRG-CRGP 972846. The Institut des Matériaux Jean Rouxel is Unité Mixte de Recherche au CNRS-Université de Nantes No. 6502.

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