
LATTICE DYNAMICS
AND PHASE TRANSITIONS

The Influence of Intercalation on the Phonon Spectrum of Titanium Dichalcogenides

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Abstract—A systematic investigation of the inelastic neutron scattering spectra is carried out for intercalation titanium diselenide compounds of the general formula $M_x\text{TiSe}_2$ ($M = \text{Cr, Fe, Ni, Ag}$). It is shown that the effect of intercalation on the phonon spectrum of the material is determined primarily by the modification of the host lattice due to the formation of Ti–M–Ti covalent centers. It is established that the lattice can undergo a substantial softening when the impurity band coincides with the Fermi level.

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1. INTRODUCTION

Intercalation of titanium dichalcogenides results in the formation of covalent centers, which are schematically described as Ti–M–Ti ($M = \text{Cr, Fe, Ni, Ag}$). These centers act as traps of free charge carriers, on the one hand, and as centers of deformation of the lattice, on the other hand. Hence, there are grounds to treat electrons localized at the Ti–M–Ti centers as impurity polarons. This interpretation is confirmed by the absence of dispersion of the impurity bands in spite of their proximity to the Fermi level (0.1–0.3 eV) [1, 2]. The temperature dependence of the degree of localization of charge carriers captured by the Ti–M–Ti centers qualitatively coincides with the theoretically predicted dependence for polarons [3]. In particular, this dependence indicates metallic conduction at high temperatures (above the temperature of thermal decomposition of polarons) and at low temperatures (the regime of heavy polarons) along with the region of the activation dependence at intermediate temperatures in the vicinity of the conductivity minimum (the regime of localized polarons). The discrepancy between theory and experiment lies in the fact that, according to theoretical concepts, the crossover from one regime to the other occurs gradually, whereas it has been established experimentally that the change in the regime is accompanied by a first-order phase transition [4]. This effect was explained by the fact that there is a feedback between the degree of localization of polarons and the elasticity of the lattice due to the influence of the density of states at the Fermi level on the permittivity of the material. An increase in the density of states at the Fermi level with increasing

degree of localization of polarons can provide the enhancement of the screening of interatomic interactions by conduction electrons and, consequently, softening of the lattice. However, since the degree of localization of polarons increases with an increase in the deformation of the lattice, there arises a positive feedback; i.e., the enhancement of the localization of polarons facilitates a further increase in the deformation of the lattice.

However, the problem is that, so far, there has been no satisfactory experimental evidence of the influence of the localization of polarons on the elasticity of the lattice. Unfortunately, the observed increase in the amplitude of thermal vibrations upon the crossover to the regime of localized polarons in Ag_xTiTe_2 [5] cannot provide convincing proof because the amplitudes of thermal vibrations are determined from an analysis of the intensities of diffraction lines, which, in turn, depend not only on the contribution of the dynamic imperfection but also on the contribution of the static imperfection of the lattice.

The most direct and consistent method for revealing the above effect is inelastic neutron scattering. This method makes it possible to determine the density of phonon states $G(\omega)$. A comparison of the densities of phonon states $G(\omega)$ for the initial material, i.e., TiSe_2 , and TiSe_2 -based compounds with metals, which are responsible for the formation of localization centers with different binding energies, provides a means for elucidating the character of the influence of the polaron

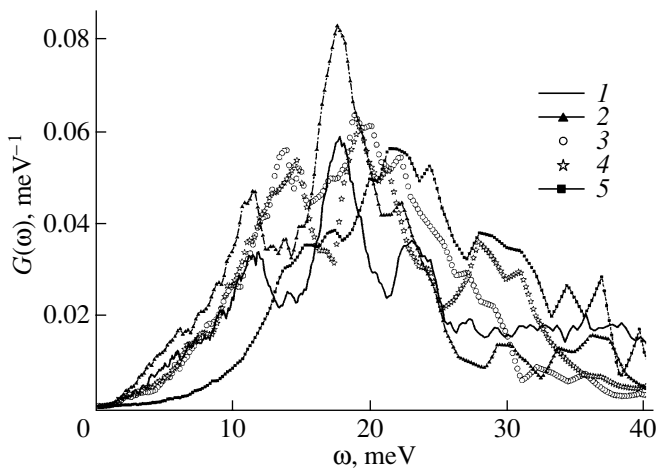


Fig. 1. Density of phonon states for samples of (1) TiSe_2 and (2–5) $M_{0.25}\text{TiSe}_2$ with $M =$ (2) Ag, (3) Fe, (4) Cr, and (5) Ni according to the calculations from the inelastic neutron scattering spectra.

state of charge carriers on the phonon spectrum of the material and, consequently, on the elastic constants.

2. SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUE

We studied materials of the general formula $M_{0.25}\text{TiSe}_2$ ($M = \text{Cr, Fe, Ni, Ag}$). The intercalant content $x = 0.25$ is the highest permissible content at which the intercalated atoms can be considered to be individual. As increase in the intercalant content above $x = 0.25$ leads to its ordering [6] and a substantial modification of the phonon spectrum of the material, which hampers the comparison of this spectrum with the spectrum of the initial compound TiSe_2 . The experiment on inelastic neutron scattering was carried out on DIN-2PI spectrometers (Joint Institute for Nuclear Research, Dubna, Russia). The measurements were performed with an incident neutron energy of 11.8 meV at room temperature. The energy resolution of the elastic line was 0.8 meV. The neutrons scattered by the sample were detected with ^{15}He detectors in the angular range 28° – 134° . The measurements of the background and vanadium for the calibration of the detectors were conducted under the same conditions. The processing of the spectra included the corrections for multiphonon scattering and neutron absorption.

3. RESULTS AND DISCUSSION

The measured spectra are depicted in Fig. 1. It is clearly seen that the phonon spectra are similar in shape and exhibit three clearly resolved peaks, whose position depends on the nature of the intercalant.

Figure 2 shows the typical dependences of the heat capacity, which were calculated from the density of

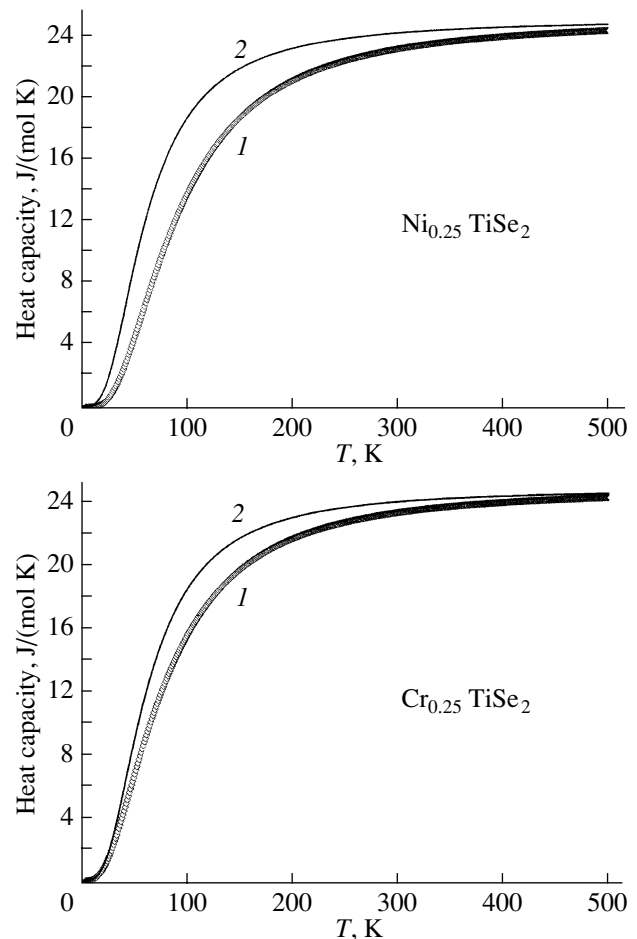


Fig. 2. Typical temperature dependences of the heat capacity calculated from the density of phonon states: (1) experiments and (2) approximation in the framework of the Debye model.

phonon states $G(\omega)$. The materials used in our experiments were chosen for the reason that there are experimental data on the heat capacity directly measured for these systems [7]. The experimental dependence of the heat capacity was approximated in the framework of the Debye model. As in the case of direct measurements, we failed to exactly approximate the experimental data in the framework of this model with a constant characteristic Debye temperature Θ_D . The deviation was described under the assumption of the temperature dependence of the quantity Θ_D . The absence of such dependence was observed only in the range of extremely low temperatures $T \leq 10$ K. Apparently, the Debye temperature Θ_D obtained in this temperature range can be considered as a temperature characterizing the total rigidity of the lattice.

We believe that the change in the rigidity of the lattice upon intercalation can be caused by the following factors: (I) the weighting of the lattice because of the incorporation of additional atoms, (ii) the aforementioned screening of the interatomic bonds by localized

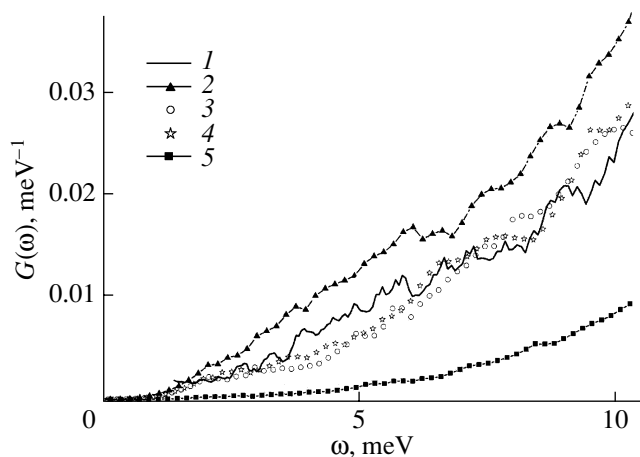


Fig. 3. Low-energy edge of the dependence $G(\omega)$ for intercalation compounds. The notation is the same as in Fig. 1.

electrons, and (iii) the total lattice deformation of the bulk compression type due to the formation of covalent bonds between the intercalant and the host lattice. Qualitatively, the nature of the dominant effect can be judged from the low-frequency edge of the dependence $G(\omega)$ for materials with different intercalants (Fig. 3).

It is clearly seen that the dependences $G(\omega)$ for TiSe_2 , $\text{Fe}_{0.25}\text{TiSe}_2$, and $\text{Cr}_{0.25}\text{TiSe}_2$ virtually coincide despite the weighting of the lattice upon incorporation of iron and chromium. However, the dependence $G(\omega)$ for $\text{Ni}_{0.25}\text{TiSe}_2$ lies considerably below despite the closeness of the atomic weights of the transition metals and their identical content in the material. It is evident that this difference can be associated with the difference in the compressive lattice deformations of the above compounds during intercalation, which reaches the highest value for the lattice of the Ni_xTiSe_2 compound.

In our earlier work [8, we showed that the compressive deformation is determined by the binding energy of the polaron band, which, in turn, depends on the ionization potential of the intercalated impurity. Therefore, the total change in the rigidity of the lattice due to intercalation and the Debye temperature Θ_D as its quantitative measure should be a function of the ionization potential of the intercalant. The dependence of the Debye temperature Θ_D on the ionization potential of the impurity is shown in Fig. 4 together with the polaron shift, i.e., the gain in the electron energy upon the formation of polarons, which characterizes the work of the compressive lattice deformation.

It can be clearly seen that the dependences of the Debye temperature Θ_D and the polaron shift of the ionization potential of the intercalant coincide. Therefore, the dominant contribution to the change in the lattice elasticity upon intercalation is made by the lattice deformation during the formation of localization centers of polaron-type charge carriers. However, Fig. 3

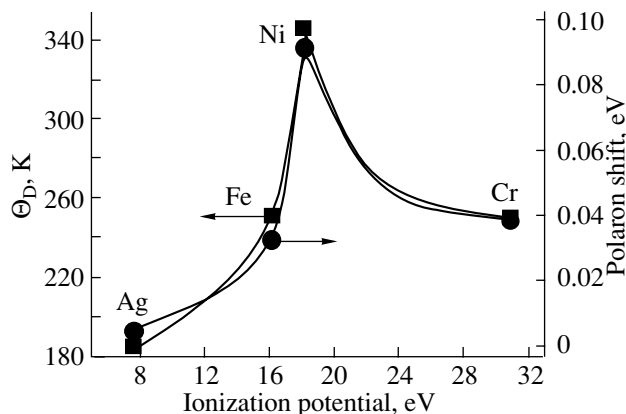


Fig. 4. Debye temperature Θ_D obtained from the inelastic neutron scattering spectra and the polaron shift calculated from the lattice strain energy upon the formation of polarons [8] as a function of the ionization potential of the intercalant.

shows that the lattice is softest in the case of incorporation of silver when the polaron shift is close to zero. The low-frequency edge of the dependence $G(\omega)$ passes to the left of the low-frequency edge of this dependence for the initial compound TiSe_2 , and the obtained Debye temperature Θ_D is equal to 196 K for $\text{Ag}_{0.25}\text{TiSe}_2$ and 221 K for TiSe_2 . Thus, the intercalation with silver leads to softening of the lattice. This phenomenon can be caused by both the larger atomic weight of silver as compared to transition metals and the lowest binding energy of the polaron band, which provides its coincidence with the Fermi level [9]. The latter fact means that the softening can be a consequence of the screening the impurity polaron band of interatomic interactions by electrons. Since the effect of weighting of the lattice is little importance for other metals, the observed softening of the lattice can be attributed to the screening effect.

4. CONCLUSIONS

The results presented in this paper clearly demonstrate that the effect of an increase in the density of states at the Fermi level upon localization of charge carriers in the form of polarons is masked by the compressive lattice deformation accompanying this process. The screening effect can be clearly observed only in the case of a negligible deformation corresponding to low binding energies of the polaron band.

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