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Pressure-induced suppression of the spin-gapped insulator phase in BaVS₃: An infrared optical study

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The metal-insulator transition in BaVS₃ was studied at ambient pressure and under hydrostatic pressure up to $p=26$ kbar in the energy range of 2.5–500 meV. The charge gap determined from the optical reflectivity was enhanced, $\Delta_{ch}(p)/k_B T_{MI}(p) \approx 12$. This ratio is independent of pressure, indicating that the character of the transition did not vary along the p - T phase boundary. Above the critical pressure, $p_{cr} \sim 20$ kbar, metallic spectra were recorded in the whole temperature range, as expected from the shape of the phase diagram.

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The class of the electron-correlation-driven metal-to-insulator transitions, characterized by an anomalously large gap parameter $\Delta/k_B T_c$, has been a hot spot of condensed matter physics during the last few decades. In most of the correlated 3d electron systems where the huge enhancement of the $\Delta/k_B T_c$ ratio (sometimes as large as ~ 30) has been observed, the MI transition is accompanied by a wide-energy-scale redistribution of the electronic states. In the relevant manganites^{1–3} and nickelates^{4,5} the typical scale of these correlation-induced spectral changes is about 1 order of magnitude higher than the charge-gap value, namely ~ 2 eV. In BaVS₃, the substantial role of the electron correlations is similarly manifested in the enhancement of the $\Delta/k_B T_c$ ratio. On the other hand, the spectral-weight redistribution observed in the optical conductivity is restricted to rather low energies, $\omega \lesssim 2\Delta$.

At ambient pressure BaVS₃ exhibits a phase transition from a high-temperature paramagnetic “bad metal” phase to a low-temperature spin-gapped insulator state at $T_{MI} \approx 70$ K.⁶ This is a second-order phase transition, as it has been pointed out recently by the comparison of the anomalies observed in different thermodynamic properties.⁷ The observation of the crystal-symmetry lowering^{8,9} in more recent x-ray experiments provided direct evidence for the second-order character of the transition at $T_{MI} \approx 70$ K.

The metallic nature of the compound is enhanced by the application of hydrostatic pressure, and the transition temperature is suppressed at an average rate of $\Delta T_{MI}/\Delta p \approx 3.4$ K/kbar.^{10,11} The critical pressure above which the metallic phase extends over the whole temperature range is $p_{cr} \approx 20$ kbar.¹¹ The suppression of the insulating phase is accompanied by a monotonic decrease of the spin gap.⁷ Moreover, the phenomenon occurring at $T_{MI} \approx 70$ K at ambient pressure shows thermodynamical analogies with the spin-Peierls transition. Its order parameter, the spin gap Δ_{sp} , scales with the transition temperature as a function of pressure according to $\Delta_{sp}/k_B T_{MI} \approx 3.6$.⁷ This indicates that the character of the phase transition does not change under pressure at least up to $p=15$ kbar.

dc conductivity measurements clearly demonstrate the opening of a charge gap (Δ_{ch}).¹² However, the magnitude and the temperature dependence of Δ_{ch} cannot be determined unambiguously; the purity of the sample has a strong influence on the dc transport in the insulating phase, and the activation energy deduced from the dc-conductivity measurements is temperature dependent. Consequently, the results obtained by different groups vary between $\Delta_{ch}=570$ K and 1120 K.^{10,13} The photoemission threshold energy reported by Nakamura *et al.*¹³ corresponds to an intermediate value, $\Delta_{ch} \approx 710$ K.

The present IR-optical study reveals the magnitude and the pressure dependence of the charge gap. Our key finding is that the $\Delta_{ch}/k_B T_{MI}$ ratio is independent of pressure. However, in contrast to $\Delta_{sp}/k_B T_{MI}$ (which is very close to the BCS ratio), the measured $\Delta_{ch}/k_B T_{MI}$ is 3 times larger. Thus, the charge gap represents a higher energy scale in the system.

The infrared reflectivity of BaVS₃ single crystals was measured in the frequency range of $\omega=2.5$ –500 meV, between room temperature and 10 K, at several pressures up to $p=26$ kbar. The incident light was unpolarized and nearly perpendicular to the rectangular (1 mm \times 3 mm), cleaved surface of the sample. The crystal preparation is described elsewhere.⁶ Since the small spot size of the beam and the high intensity in the far-infrared (FIR) range were crucial requirements for this study, most of the measurements were made at the U10A beamline of the National Synchrotron Light Source of the Brookhaven National Laboratory, with a Bruker 66v/S spectrometer. At ambient pressure the sample was mounted on the cold finger of a helium-flow cryostat. The reflectivity data were referenced to the reflectivity of a gold mirror, which was also mounted on the cryostat. Some of the data below 6 meV were taken in a Bruker 113v spectrometer, using the internal source, with an Au film evaporated to the surface of the sample to act as a reference. The same crystal was also studied in a custom-designed self-clamping pressure cell. Optical access was achieved through a cylindrical natural diamond, with wedged plane surfaces to eliminate interference fringes and to facilitate reference mea-

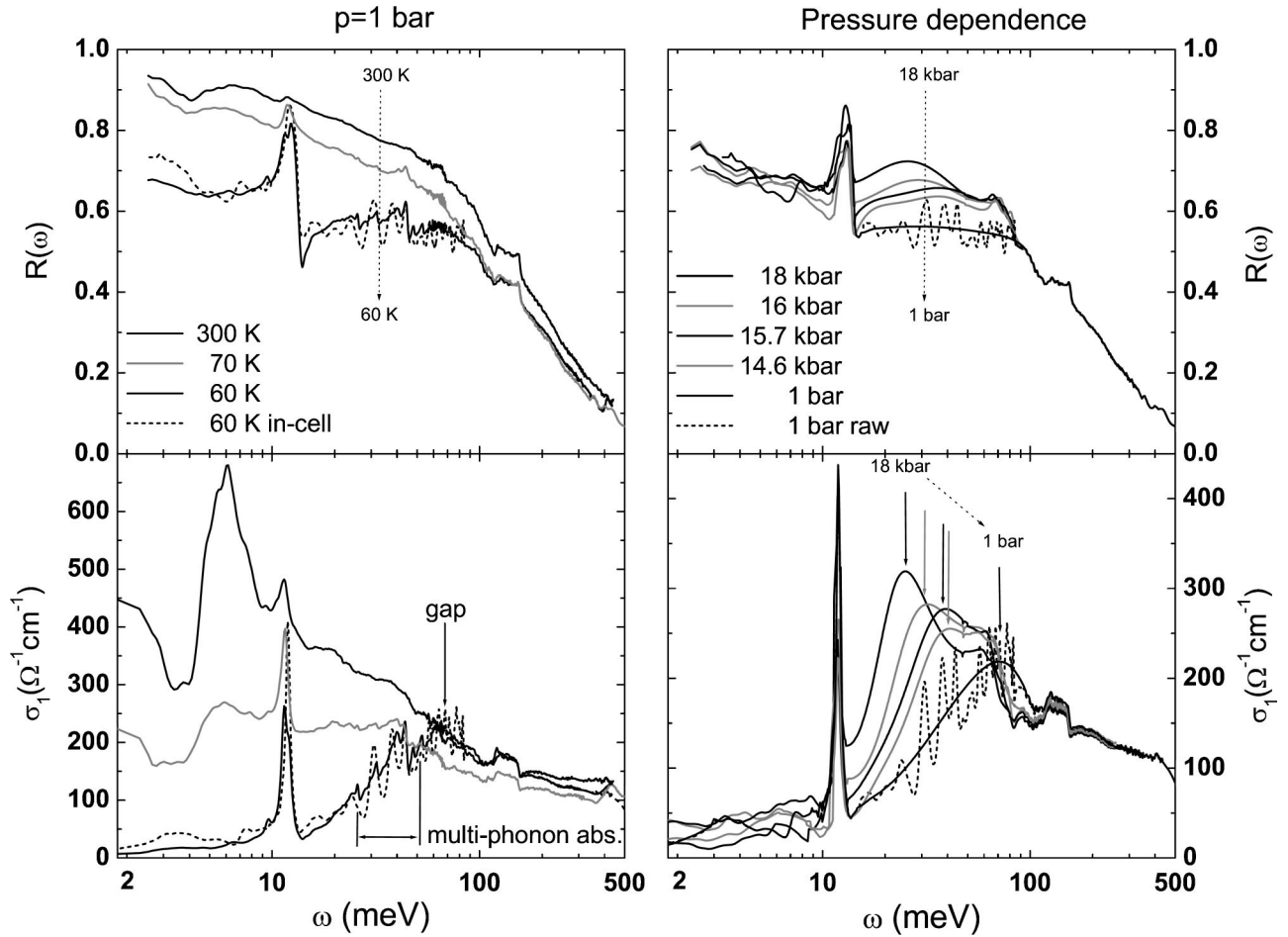


FIG. 1. Left panel: The temperature evolution of the reflectivity and conductivity spectra of BaVS₃ through the metal-insulator transition at ambient pressure. The values of the gap and the multiphonon branch just below the gap are indicated by arrows. For comparison, the data obtained at $T=60$ K inside of the pressure cell are also plotted. Right panel: The reflectivity and conductivity spectra in the insulating phase of BaVS₃ at several pressures measured at ~ 10 K below the metal-insulator transition. At ambient pressure both the “1 bar raw” spectra (which is evaluated by Eq. (1) and referred to as “60 K in-cell” in the left panel) and the smoothed curves are shown. In the conductivity plot the arrows indicate the energies identified with the gap values. Note that the scale of the conductivity axis is enlarged relative to the ambient pressure case.

measurements. The large (1.5 mm) window size and the absence of low-frequency absorption allowed investigations down to $\omega=2.5$ meV=20 cm⁻¹. We used the light reflected from the outer surface of the diamond (vacuum-diamond boundary) as a reference signal. The sample was mounted on the inner surface of the diamond, and the angle of wedging between the two surfaces allowed a clear separation of the reference and sample reflections. Besides the optical access, an electrical leadthrough was also implemented, and the pressure was monitored *in situ* by an InSb sensor. The pressure cell was also cooled by the He-flow cryostat.

The temperature dependence of the ambient-pressure optical spectra, shown in the right panel of Fig. 1, clearly shows the characteristics of the metal-insulator (MI) transition. Above T_{MI} the low-energy reflectivity tends towards unity, $R \rightarrow 1$; thus a metallic conductivity is observed. In contrast, below T_{MI} the low-energy reflectivity becomes considerably smaller and frequency independent. Furthermore, due to the vanishing electronic screening the phonon resonances sharpen. The dominant phonon peak around 12 meV is

clearly observable below 70 K at ambient pressure and at every pressure, as long as the metal-to-insulator transition takes place. Similarly to the isostructural BaTiS₃ and BaNbS₃,¹⁴ this peak is due to two closely centered modes. Both of them correspond to the motion of the barium relative to the sulfur octahedron and the embedded atom (in our case the vanadium). The multiphonon excitations at higher energies (25–50 meV) are related to the motion of the vanadium relative to the surrounding sulfur octahedron.

In terms of the optical conductivity, the key finding is the complete suppression of the low-energy spectral weight below T_{MI} , due to the development of the charge gap. At high frequencies the difference between the metal and the insulator disappears, and above ~ 100 meV all the curves essentially converge. Below the phase transition, however, $\sigma(\omega)$ shows a maximum with an energy that is identified with the gap value, $\Delta_{ch} \approx 66$ meV=750 K. We only note here that the temperature dependence of the charge gap is very weak below $T=60$ K; therefore this value essentially corresponds to $\Delta_{ch}(T=0)$. The detailed temperature dependence of the opti-

cal conductivity, together with the analysis of the low-energy (~ 5 meV) feature in the metallic spectra, will be published elsewhere. Even though alternative ways¹⁵ can be followed to evaluate the gap from the optical conductivity, the above definition is justified by the good agreement with the gap value derived from the photoemission data of Ref. 13. Note that the single-particle excitations below the gap, if they exist, cannot be distinguished from the contribution of a multiphonon absorption in the 25–50 meV range; thus in contrast to Ref. 15, in our case the fitting of the gap profile in $\sigma(\omega)$ cannot be carried out. Our procedure for the gap identification is also supported by the results of dc-conductivity measurements performed in the same pressure range (see later).

The right panel of Fig. 1 shows the optical spectra measured under hydrostatic pressure. The evaluation of the results obtained inside of the pressure cell was done the following way. In order to eliminate interference fringes due to the thin film of the pressure medium formed between the sample and the diamond, at each pressure we calculated the ratio of the insulating reflectivity and the metallic phase reflectivity. Then we evaluated the absolute reflectivity of the insulator according to

$$R_{abs}^I(p) = \frac{R^I(p)}{R^M(p)} R_{abs}^M, \quad (1)$$

where $R^I(p)$ and $R^M(p)$ are the raw reflectivity data obtained at a given pressure ~ 10 K below and above T_{MI} , respectively, and R_{abs}^M is the absolute reflectivity in the ambient-pressure metallic phase measured out of the pressure cell. This evaluation does not influence the structure of the spectra since, (i) in the metallic state of BaVS₃ the reflectivity has a weak and monotonous temperature dependence with a relative change $\leq 15\%$ at any of the investigated pressures, and (ii) the high-temperature dc conductivity is not very sensitive to the pressure, as $\sigma_{dc}(p=22 \text{ kbar})/\sigma_{dc}(p=1 \text{ bar}) \approx 1.3$ at room temperature.¹¹ After calculating the reflectivity by Eq. (1) some remains of the interference fringes (mixing with the phonon peaks) are still superimposed on the data, as it is shown in case of the ambient-pressure measurement performed inside of the pressure cell. These spectra are referred to as the “60 K in-cell” and “1 bar raw” curves in the left and right panels of Fig. 1, respectively. The agreement between the ambient-pressure-insulating spectra obtained inside and out of the pressure cell is clearly demonstrated in the left panel. In order to better visualize the results, we smoothed out this oscillation in the reflectivity by interpolation and then applied the Kramers-Kronig transformation. This step effectively lowered the frequency resolution, and it resulted in the smearing out of the phonon peaks in the range of 25–50 meV; however, it allowed a better determination of the charge gap.

The charge gap was reduced by the applied pressure as the maxima in the conductivity spectra were shifted to lower frequencies. At $p=26$ kbar neither the opening of the gap nor the sharpening of the 12 meV phonons could be detected, indicating that the material remained metallic. This is in

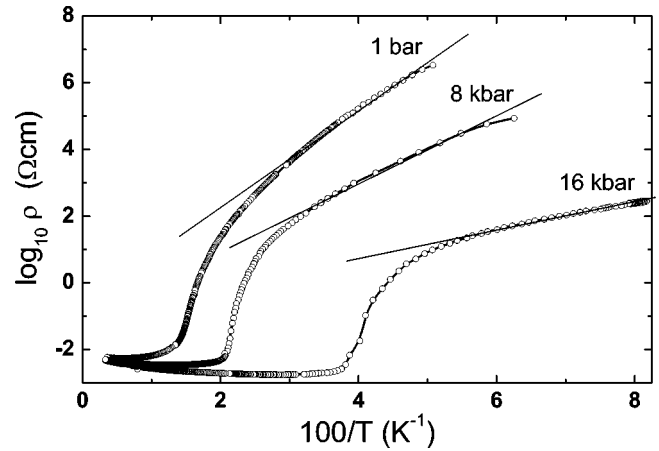


FIG. 2. Arrhenius plot for the resistivity of BaVS₃ at three different pressures: 1 bar, 8 kbar, and 16 kbar. The straight lines indicate the fitting of the activation energy.

agreement with the shape of the p - T phase boundary and the value of the critical pressure $p_{cr} \approx 20$ kbar determined by resistivity measurements.¹¹

In contrast to the optical gap, the activation energy derived from the dc-conductivity experiments is influenced by the impurity concentration. In a separate study we investigated the dc transport of several samples under pressure. The resistivity of the cleanest sample (plotted in Fig. 2) increased by 9 orders of magnitude from T_{MI} down to $T=20$ K at ambient pressure. Although its temperature dependence slightly deviated from the Arrhenius law, one can estimate the gap within a 30% error and find $\Delta_{ch} = 690 \pm 100$ K. Both the magnitude and the pressure dependence of the charge gap, determined from the resistivity measurements, agree fairly well with the results of the IR study, as shown in Fig. 3. In the $p=0$ –18 kbar range the following scaling relation holds:

$$\frac{\Delta_{ch}(p)}{k_B T_{MI}(p)} \approx 11.6. \quad (2)$$

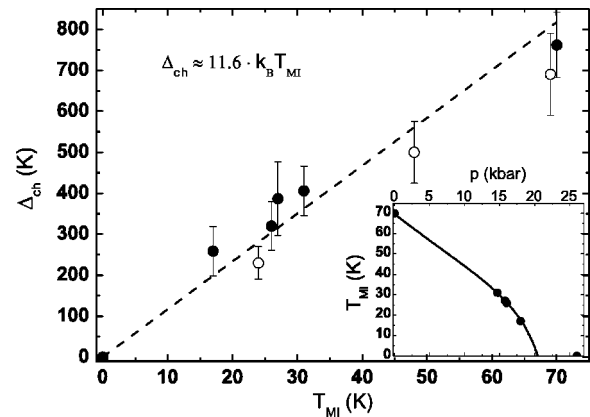


FIG. 3. The charge gap vs the transition temperature as derived from the optical (solid symbols) and the dc transport (open symbols) experiments. The dashed line corresponds to Eq. (2). The continuous line in the inset is the p - T phase boundary from Ref. 11, and the dots show the pressures investigated in the present study.

Finally, we briefly discuss two basic effects that could be responsible for the large value of the gap parameter, $\Delta_{ch}/k_B T_{MI} \approx 12$. One possibility is that the charge gap was affected by the electron-electron interaction. Such a correlation-driven enhancement of the gap is thought to be present in several manganites such as $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ ($x \geq 0.6$),¹ $\text{Bi}_{1-x}\text{Ca}_x\text{MnO}_3$ ($x=0.74-0.82$),² and $\text{Pr}_{0.6}\text{Ca}_{0.4}\text{MnO}_3$ (Ref. 3) and nickelates like NdNiO_3 (Ref. 5) where the gap parameters are ~ 20 , ~ 9 , ~ 10 , and ~ 20 , respectively.

Another explanation is that the transition temperature could be much higher, but strong fluctuations suppressed the development of the ordered state. These fluctuations might have been induced by the competition of different types of orderings such as in $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ ($x \approx 0.5$), where ferromagnetic and charge orders (CO) coexist in a limited region of the T - x phase diagram.¹ A wide precursor range can also arise from the low dimensionality of the system, as it is the case in many CDW or SDW compounds or in $\text{La}_{1.67}\text{Sr}_{0.33}\text{NiO}_4$, where the presence of fluctuating charge stripes was observed well above T_{CO} .⁴

In conclusion, our far-infrared optical study revealed the evolution of the charge gap in BaVS_3 as a function of hy-

drostatic pressure. The spectral weight transfer observed in the optical conductivity upon the metal-to-insulator transition was located at low energies, typically $\omega \leq 2\Delta_{ch}$. It is shown that the charge gap was suppressed by the applied pressure proportional to the transition temperature T_{MI} . The gap parameter was anomalously large, $\Delta_{ch}(p)/k_B T_{MI}(p) \approx 12$, indicating the substantial role of electron correlations in driving the metal-insulator transition in BaVS_3 .

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¹²In our notation Δ_{ch} is the entire energy needed for the charge excitation, not its half. The same convention is followed in case of the spin gap Δ_{sp} .

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