

## Pressure dependence of the spin gap in BaVS<sub>3</sub>

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We carried out magnetotransport experiments under hydrostatic pressure in order to study the nature of the metal-insulator transition in BaVS<sub>3</sub>. Scaling relations for  $\rho(T,H,p)$  are established and the pressure dependence of the spin gap is determined. Our results, in conjunction with a reanalysis of earlier specific-heat and susceptibility data, demonstrate that the transition is weakly second order. The nature of the phase diagram in the  $T$ - $p$ - $H$  space is discussed.

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There has been great progress in understanding metal-to-insulator transitions which are accompanied by magnetic ordering and/or structural distortions.<sup>1</sup> In contrast, “pure” Mott transitions which do not involve any apparent change of symmetry, remains poorly understood. The suppression of magnetic order is usually due to frustration, or possibly orbital fluctuations. Differences in lattice structure and the subspace of the relevant orbitals make each of these systems unique.

The recent availability of single-crystal specimens of BaVS<sub>3</sub> has brought fresh insights,<sup>2,3</sup> but understanding the character of its Mott transition, and the nature of the low-temperature phases, remains a challenging problem. Under atmospheric pressure, the material undergoes a metal-to-insulator transition at  $T_{MI}=69$  K from a  $T>T_{MI}$  bad metallic state to a  $T<T_{MI}$  insulator. There is a further phase transition at  $T_X=30$  K,<sup>2,4</sup> and it is now understood that long-period magnetic order sets in here.<sup>5</sup> However, in this paper we will be concerned with the intermediate ( $T_X<T<T_{MI}$ ) insulating phase (we will call this the insulating phase) which is isostructural with the metallic phase, and has no magnetic long-range order.<sup>6,7</sup> It is a singlet insulator<sup>8</sup> characterized by a singlet-triplet gap. Various measurements give varying estimates for the spin gap: NMR/NQR (Ref. 4) suggested  $\Delta_S=22$  meV, but according to inelastic neutron-scattering studies  $\Delta_S\sim 10$  meV is more likely.<sup>9</sup> A remarkable feature of BaVS<sub>3</sub> is that the Mott transition is associated with the appearance of a spin gap. It follows that an applied magnetic field should tend to stabilize the  $T>T_{MI}$  paramagnetic phase and eventually fully suppress the metal-insulator transition at a critical field which is of the order of the spin gap. The possibility of a field-induced shift in the transition is expected to be detectable by studying the magnetoresistance<sup>10</sup> which happens to offer a way to measure the pressure dependence of the spin gap. In this paper we show that the Mott transition continues to coincide with the onset of a spin gap.

Our paper has two main points. First, we use magnetoresistivity measurements to determine the pressure dependence of the spin gap up to  $p=15$  kbar. Here we closely follow Booth *et al.*<sup>11</sup> who did a similar analysis for  $p=1$  bar. However, we managed to improve their procedure by dropping some of the simplifying assumptions, and derive corresponding statements from the data instead. Second, we use our

fresh data in conjunction with previous susceptibility<sup>2</sup> and specific-heat<sup>12</sup> data to discuss the properties of the thermodynamic potential  $G(T,p,H)$ , and determine the character of the metal-insulator transition. In contrast to previous claims,<sup>13</sup> we conclude that it is a genuine second-order phase transition.

Single crystals of BaVS<sub>3</sub> were grown by the tellurium flux method. The samples used in this work come from the same batch as those investigated in Ref. 2. The resistivity measurements under pressure were performed in a nonmagnetic copper-beryllium cell using kerosene as the pressure medium. The magnetoresistance (MR) was studied in two ways: by magnetic-field sweeps at various temperatures and by measuring the temperature dependence of the resistivity in zero and in high magnetic field ( $H_{max}=120$  kG). By simultaneous application of carbon glass and capacitive thermometers the overall uncertainty of temperature was reduced below  $\pm 0.05$  K.

Figure 1 shows representative  $\rho(T)$  curves measured at various pressures both in  $H=0$  and  $H=120$  kG magnetic field. In accordance with earlier observations,<sup>3,13</sup> the domi-

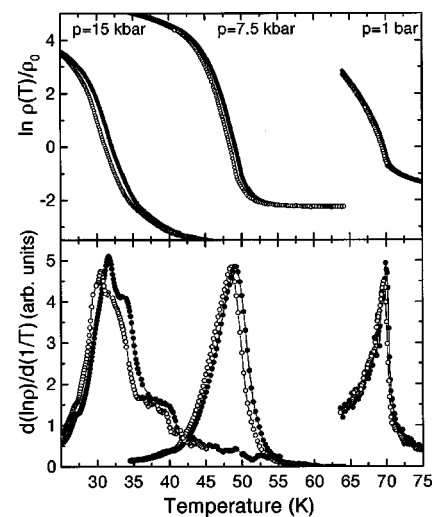


FIG. 1. Temperature dependence of the normalized resistivity (upper panel) and its logarithmic derivative (lower panel) at various pressures. Solid and open circles are for zero-field and  $H_{max}$ , respectively. The sharp peaks define the transition temperatures at  $p=1$  bar, 7.5 kbar, and 15 kbar.

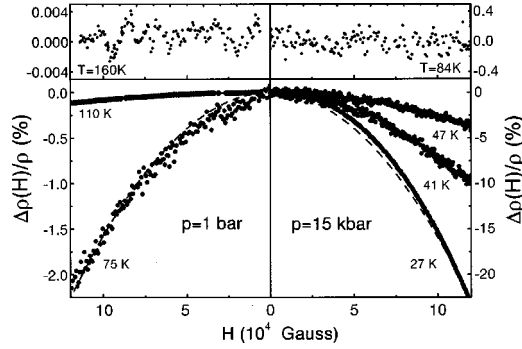


FIG. 2. Magnetic-field dependence of the resistivity at various temperatures at  $p=1$  bar, and  $p=15$  kbar. The dashed curves indicate the quadratic fit to the data. Note the different scales in the upper panel.

nant effect is the pressure induced reduction of the transition temperature. The influence of the applied magnetic field is comparatively weak. It is an excellent approximation that for all pressures the resistivity depends on the magnetic field only through the field-induced shift of  $T_{MI}$ ; the resistivity in  $H_{max}$  is the shifted counterpart of the zero-field one. It seems a plausible assumption that any smaller field has the same effect on the resistivity, i.e.,

$$\rho(T, H, p) = \rho[T - T_{MI}(H, p), p]. \quad (1)$$

$T_{MI}$  itself can be determined with a high accuracy by the logarithmic derivative of the resistivity,  $\partial(\ln \rho)/\partial(1/T)$ , as shown in the lower panel of Fig. 1.

The field dependence of the transition temperature is weak, but it is increasing with increasing hydrostatic pressure:  $\Delta T_{MI}(H_{max})$  grows from 0.35 K at ambient pressure to 0.9 K at 15 kbar.

As expected from the data shown in Fig. 1, the magnetoresistance becomes large in the vicinity of the metal-insulator transition. Field sweeps performed at constant temperatures revealed a quadratic magnetoresistance for each pressure,

$$\Delta\rho(T, H, p) \propto H^2. \quad (2)$$

Figure 2 shows representative curves for  $p=1$  bar, and  $p=15$  kbar. Note that far above the transition the magnetoresistance is strongly reduced (upper panels). In fact, for  $T > 2T_{MI}$ , no effect can be observed, confirming that the dominant term in the magnetoresistance is due to the field dependence of  $T_{MI}$  and any other contribution to  $\Delta\rho$  is below the detection limit.

Taken in conjunction with Eq. (1), Eq. (2) shows that at the field strengths available to us,  $\Delta T_{MI}(H)$  is purely quadratic:

$$\Delta T_{MI}(p, H) = -a(p)H^2. \quad (3)$$

In the sense of Eq. (1), at any given pressure  $\Delta\rho(H)$  can be expanded in terms in  $\Delta T_{MI}(H)$ , or effectively in powers of  $H$ . Up to second order in  $\Delta T_{MI}$

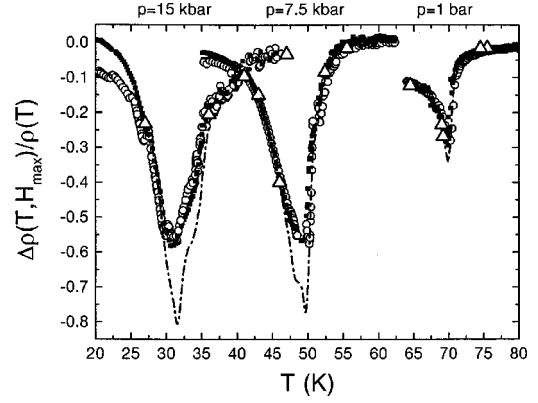


FIG. 3. Analysis of the magnetoresistance at various pressures. Full symbols:  $\Delta\rho(T, H_{max})/\rho(T)$  measured by thermal sweeps in presence of magnetic field, triangles: results of measurements by magnetic-field sweeps at selected temperatures, dashed lines: first-order calculation according to Eq. (4); open circles: second-order calculation from the zero field  $\rho(T)$  curves according to Eq. (4).

$$\begin{aligned} \Delta\rho(T, p, H) &= -\left(\frac{\partial\rho(T, p)}{\partial T}\right)_{H=0} \Delta T_{MI}(p, H) \\ &\quad + \frac{1}{2}\left(\frac{\partial^2\rho(T, p)}{\partial T^2}\right)_{H=0} [\Delta T_{MI}(p, H)]^2 \quad (4) \\ &= a(p)\left(\frac{\partial\rho(T, p)}{\partial T}\right)_{H=0} H^2 \\ &\quad + \frac{1}{2}a^2(p)\left(\frac{\partial^2\rho(T, p)}{\partial T^2}\right)_{H=0} H^4. \quad (5) \end{aligned}$$

Though  $\Delta T_{MI}(H)$  contains no fourth-order shift, the  $\propto H^4$  term appearing in Eq. (5) is not negligible because  $\rho(T)$  is a sharply varying function of  $T$  near  $T_{MI}$ .

The consistency of our scheme can be verified, since the quantities on either side of Eq. (4) can be measured independently. In Fig. 3 full squares show the directly measured  $\Delta\rho(T, H_{max})/\rho(T)$ , as obtained from the difference of the  $\rho(T)$  curves measured in 120 kG, and in zero field, respectively. This set of data is to be compared to the curves calculated from Eq. (4) using the partial derivatives of resistivities measured at zero field, and inserting the value of  $\Delta T_{MI}(H_{max})$  determined experimentally (Fig. 1, lower panel). There is no free parameter in the calculation. The results of expanding to order  $(\Delta T_{MI})^2$  are shown in Fig. 3 by open circles. The agreement is good. It is clear that the second term of the expansion is necessary to describe the results near  $T_{MI}$ , and that it is also sufficient.

The first-order expansion (shown by dashed line in Fig. 3) gives already a good approximation except in the closest vicinity of the transition. In the range where the first-order approximation is valid,

$$\Delta\rho(H, p) = \left(\frac{\partial\rho(T, p)}{\partial T}\right)_{H=0} \Delta T_{MI}(H, p) = -\beta(p)H^2, \quad (6)$$

i.e., the magnetoresistance curves determined by field sweeps scale to the magnetic field dependence of the transition temperature. The magnetoresistance has been determined at several temperatures at each pressure; the corresponding values at  $H_{\max}$  are shown in Fig. 3 by open triangles. This reasserts that the field dependence of the transition temperature  $T_{\text{MI}}(H)$  is quadratic in  $H$  for all pressures.

Equation (3) can be brought to the dimensionless form

$$\frac{\Delta T_{\text{MI}}(H)}{T_{\text{MI}}} = -\gamma \left( \frac{gS\mu_B H}{k_B T_{\text{MI}}} \right)^2, \quad (7)$$

where  $S=1/2$  and  $g=2$ . The sensitivity of the transition to the applied field is characterized by the constant  $\gamma$ . The magnetoresistance results yield  $\gamma=0.45$ , *independently of pressure*.

We note that an analogous relationship describes the suppression of the spin-Peierls transition by a magnetic field, with very similar values of  $\gamma$ . On the theoretical side, Bulaevskii *et al.*<sup>14</sup> predicted  $\gamma=0.44$ , while Cross<sup>15</sup> found  $\gamma=0.38$ . Later experiments established that  $\gamma=0.41 \pm 0.05$  is universal both for organic<sup>16</sup> and inorganic<sup>17</sup> compounds. Since the magnetic field acts by making an antiparallel alignment of magnetic moments less favorable, we guess that the nature of short-range correlations in BaVS<sub>3</sub> is similar as in spin-Peierls systems (even though no static distortion is involved in our case).

Another dimensionless form of Eq. (3) is obtained by introducing the pressure-dependent spin gap  $\Delta_S(p)$ :

$$\frac{\Delta T_{\text{MI}}(H)}{T_{\text{MI}}} = -\alpha \left( \frac{g\mu_B S H}{\Delta_S(p)} \right)^2 \quad (8)$$

assuming that it is related to a characteristic magnetic field  $H_c$  via the corresponding Zeeman energy. We derived the coefficient  $\alpha=1.0 \pm 0.1$  by accepting the ambient pressure value of the spin gap  $\Delta_S(p=1 \text{ atm})=10 \text{ meV}$ .<sup>9</sup>  $H_c$  can be also understood as the critical magnetic field which would suppress the metal-to-insulator transition completely but one has to bear in mind that only the weak-field behavior is known (with our assumption  $H_c=1700 \text{ kG}$ ). Analyzing their  $p=1 \text{ atm}$  magnetoresistivity data, Booth *et al.* found  $H_c=2600 \text{ kG}$  (175 K).<sup>11</sup> Let us note, though, that Booth *et al.* postulated a specific (elliptical) form of the phase boundary in the  $T$ - $H$  plane, and thus in their scheme,  $\alpha$  is fixed by geometry rather than measured.

Equation (8) allows us to determine the pressure dependence the spin gap  $\Delta_S(p)$  directly from the measured  $T_{\text{MI}}$  shifts (Fig. 1). They can also be derived from magnetoresistance measurements performed at constant temperatures using Eqs. (6) and (8) which relate  $\alpha$  to  $\beta(p)$ . The results are shown in Fig. 4 where the pressure dependence of the transition temperature is also presented. We found that within the experimental resolution the spin gap of the insulating state scales with the transition temperature according to  $\Delta_S(p) \approx 1.7 \cdot k_B T_{\text{MI}}(p)$ .

The transition temperature  $T_{\text{MI}}$  is marked as a peak in the  $d(\ln \rho)/d(1/T)$  vs  $T$  plots but it has been long disputed whether it belongs to a true thermodynamic transition. The early suggestion of a weakly first-order transition<sup>6</sup> was discarded in favor of a smooth conductor-to-insulator

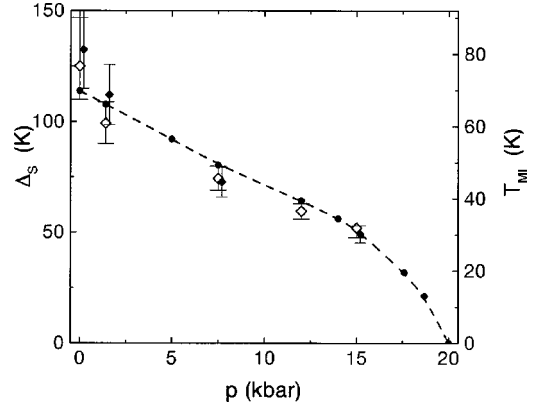


FIG. 4. The pressure dependence of the spin gap (diamonds, left-hand scale) scales with that of  $T_{\text{MI}}$  (solid circles connected by broken line, right-hand scale). The spin gap determined from the shift of the transition temperature and from the magnetoresistance is shown by open and full diamonds, respectively.

crossover.<sup>13</sup> This might have been either of the kind of the supercritical behavior observed near the critical point of the  $V_{2-x}Cr_xO_3$  system,<sup>1</sup> or like the behavior of Kondo insulators.<sup>18</sup> However, we argue against this interpretation, and show that the transition is a genuine phase transition. As to the first alternative, the nearness to a critical-point situation should be an accidental feature and we should expect that changing the parameters drives either towards a first-order phase transition, or well away from the critical point. However, the resistivity curves show that essentially the same transition is taking place at all pressures up to  $p_{\text{cr}}=20 \text{ kbar}$ ,<sup>3,19</sup> and/or in accessible magnetic fields. As to the second possibility, the crossover from the low-temperature insulator to the high-temperature conductor in Kondo lattices can be generically continuous, because the insulating ground state does not violate Luttinger's theorem. Actually, this possibility cannot be trivially refuted for BaVS<sub>3</sub>, because the unit cell contains two V sites, i.e., an even number of  $3d$  electrons. However, we explicitly show below that there is a phase transition at  $T_{\text{MI}}$ .

Unfortunately, at  $p>1 \text{ bar}$ , only resistivity data are known, thus the following discussion has to be restricted to the ambient pressure case. The lowest-order quantities which clearly show nonanalytic behavior are the temperature derivatives of the susceptibility components:  $d\chi_c/dT$  and  $d\chi_a/dT$  have large jumps at  $T_{\text{MI}}$ .<sup>2,20</sup> If it were only for these,  $\partial\chi/\partial T = -(\partial^3 G/\partial T \partial H^2)$  being a third derivative of the thermodynamic potential  $G(T,p,H)$ , one might have suspected that the transition is of third order. We should, however, seek to relate  $\Delta(\partial\chi/\partial T) = (\partial\chi_1/\partial T) - (\partial\chi_M/\partial T)$  to other thermodynamic quantities by general reasoning.<sup>21</sup>

The thermodynamic potential  $G(T,p,H)$  must be continuous across the transition:  $f(T,p,H) = G_I(T,p,H) - G_M(T,p,H) \equiv 0$  along the phase boundary given by Eq. (3):  $T_{\text{MI}}(H) = T_{\text{MI}}^0 - a_0 H^2$ , where  $T_{\text{MI}}^0 = T_{\text{MI}}(p=1 \text{ bar})$ , and  $a_0 = a(p=1 \text{ bar})$ . Expanding  $f$  to fourth order in  $H$ , and considering that the entropy and the linear susceptibility are continuous across the transition, and that neither of the phases has spontaneous magnetization  $M_I(T,H=0) = M_M(T,H=0) = 0$ , we are left with the relationship

$$\Delta\left(\frac{\partial\chi}{\partial T}\right) = \frac{a_0}{T}\Delta C + \frac{1}{12a_0}\Delta\chi^{(3)}. \quad (9)$$

The discontinuity of  $\partial\chi/\partial T$  has to be balanced by a combination of the discontinuities of the specific heat  $C$ , and the nonlinear susceptibility  $\chi^{(3)}$ .

We have measured  $\Delta(\partial\chi/\partial T)$ ,<sup>2</sup> and  $a_0$ .  $\Delta C$  and  $\Delta\chi^{(3)}$  have to be taken from published data. Imai *et al.*<sup>12</sup> find a strong anomaly at  $\sim 69$  K in the electronic specific heat which they chose to identify as a sharp peak rather than as a discontinuity but this interpretation is not compelling. We have made a plot using their published data points and find that they allow that part of the peak height is made up by a discontinuity (Fig. 5, left). Our fit with  $(C_I - C_M)/C_M = 1.4$  is certainly somewhat arbitrary, but the correct value cannot be very different.

Though the so obtained  $\Delta C$  is of the order of magnitude required by Eq. (9), a fraction of  $\Delta(\partial\chi/\partial T)$  has to be matched by  $\Delta\chi^{(3)}$ . High-field magnetization data have been published by Booth *et al.*<sup>11</sup> The authors emphasize that the magnetization curves are essentially linear, but in fact the data shown in their Fig. 2 are compatible with a size of the discontinuity  $\Delta\chi^{(3)} < 0$ , which is sufficient to satisfy Eq. (9).

The character of the transition is described by Eq. (9) which contains both second and third derivatives of  $G$ . For this reason, one might say that the continuous phase transition is “weakly second order.” In any case, the existence of a surface of continuous phase transitions in the  $T$ - $p$ - $H$  space strongly suggests that there is a distinct nonmagnetic insulating phase which differs from the metallic phase not in transport properties only, but also in the sense of possessing a hidden order.

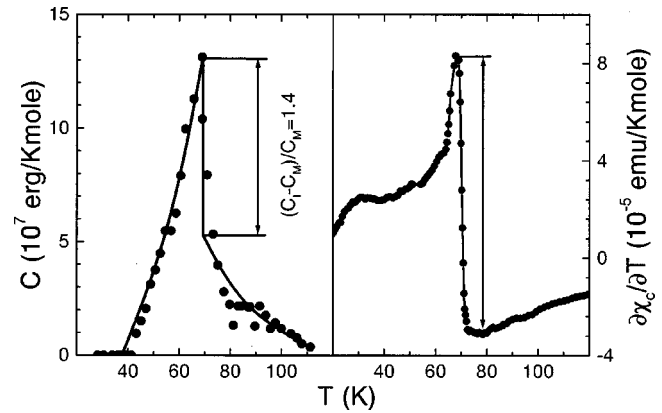


FIG. 5. Comparison of the the specific heat (based on data taken from Ref. 12) and temperature derivative of the  $c$ -axis susceptibility (based on Ref. 2). The lines are guide to the eye.

In conclusion, magnetotransport measurements under pressure were performed on single crystals of  $\text{BaVS}_3$  in order to study the nature of the metal-insulator transition. We determined the pressure dependence of the spin gap in the insulating phase and showed that  $\Delta_S$  scales with the transition temperature. We discussed the nature of the phase diagram and pointed out that the metal-insulator transition is not a smooth crossover but a genuine phase transition.

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<sup>8</sup>The finding of the susceptibility anisotropy (Ref. 2) shows that spin-orbit coupling is not negligible, and the notion of a singlet is only approximate.

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<sup>10</sup>In spite of a general resemblance, the case of  $\text{BaVS}_3$  is just the opposite of that of CMR manganites: for those, the nearness to the ferromagnetic state drives the transition, while here, it is the nonmagnetic nature of the insulating phase.

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<sup>19</sup>Actually, it is possible that at the highest pressures, there is a metal-to-magnetic-insulator transition. We have not seen any sign of this up to  $p = 15$  kbar.

<sup>20</sup>The difference between the  $d\chi_c/dT$  and  $d\chi_a/dT$  discontinuities being of the order of 10%, we neglect anisotropy in the discussion.

<sup>21</sup>For Ising antiferromagnets, the Fisher relation [M. E. Fisher, Philos. Mag. **7**, 1731 (1962)]  $a_0 C = d(\chi T)/dT$  has long been used to establish a relationship between the divergence of  $C$ , and the infinite slope of  $\chi$  at  $T_N$ . The relationship holds for strongly uniaxial systems, but would not apply to nearly isotropic systems like  $\text{BaVS}_3$ . It is nevertheless interesting that if we assumed that  $d\chi/dT$  has a finite discontinuity, then also Fisher’s equation would say it is related to a jump of  $\Delta C$ .