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High-pressure resistance study of NpSb up to 23 GPa

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The resistance versus pressure of NpSb single crystals has been measured up to 23 GPa and as a function of temperature from 1.3 to 300 K. Up to 2.3 GPa the Néel temperature, T_N, is found to decrease at a rate of about -11.5 K/GPa. We suggest that the direct effect of pressure on the spin may play a significant part in this variation. Between 2.3 and 2.7 GPa a dramatic change in the resistance versus temperature behavior below T_N indicates some electronic or magnetic transformation in NpSb. At higher pressure the NaCl to tetragonal structural phase transition is observed by a decrease in the room temperature resistance and a maximum in the low-temperature resistance. The transition pressure is determined to be between 6 and 8 GPa and the transition shows considerable hysteresis on releasing the pressure. This is compared to previous data from high-pressure x-ray diffraction experiments which show a higher transition pressure. The high-pressure phase seems likely to be nonmagnetic and we show indirect evidence for delocalization of the $5f$ electrons at the phase transition.

I. INTRODUCTION

NpSb belongs to the family of the neptunium monopnictides (NpX with X=N,P,As,Sb,Bi) which all crystallize in the simple-cubic NaCl structure. At normal pressure the Np-Np spacing is greater than the Hill limit,[1] the critical distance where the $5f$-$5f$ overlap leads to delocalization of the $5f$ electrons. The $5f$ electrons are therefore localized and NpSb orders magnetically in the antiferromagnetic (AF) triple-**k** type-I structure.[2] From the electronic point of view NpSb is a semimetal and the room-temperature resistivity exhibits the relatively high value of about 1.5 mΩ cm. The temperature dependence of the resistivity of NpSb has previously been measured and is shown as an inset in Fig. 1.[3] Above the Néel temperature $T_N=200$ K the resistivity exhibits a negative slope typical of a Kondo lattice behavior. Below T_N a sharp increase in the resistivity is observed. A similar behavior is observed in NpAs and NpBi and has been attributed to a reduction of the number of carriers due to the onset of the triple-**k** AF order which is thought to be particularly effective.[3]

The application of pressure is a good way of reducing the Np-Np spacing and increasing the $5f$ overlap. The $5f$ electrons can eventually delocalize and become bonding leading to phase transitions to lower symmetry structures and large volume collapses. In the case of NpSb, high-pressure x-ray diffraction at room temperature shows a phase transition to a distorted CsCl structure at around 12 GPa, although whether this transition can be associated with the delocalization of the $5f$ electrons is not sure.[4] If this phase transition does involve the delocalization of $5f$ electrons some signature should be present in the electrical resistance. High-pressure resistance measurements can therefore be hoped to provide insights into the electronic, magnetic, and structural changes under pressure.

II. EXPERIMENT

The experimental setup has been developed from an existing technique[5] and described in detail elsewhere.[6] Because of the radiotoxicity of the sample all the loading

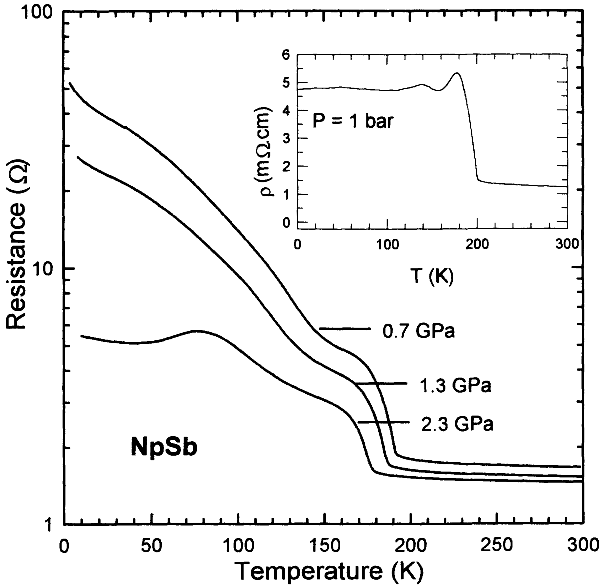

FIG. 1. Resistance vs temperature curves of NpSb at pressures up to 2.3 GPa. Please note that the R scale is logarithmic. The inset shows the ambient pressure measurement of Pleska (1990).

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operations are carried out in a glove box. The press is then transferred in a sealed container to a liquid-He cryostat where the temperature can be scanned from approximately 1.3 K to room temperature. Thin platelets of NpSb of dimensions approximately 0.6×0.2×0.04 mm were cleaved from a larger single crystal, the growth of which has been described elsewhere.[7] The sample, together with a piece of Pb thin foil, was embedded in steatite to ensure quasihydrostatic conditions and compressed between two sintered diamond Bridgman anvils. The sample resistance was measured with a four-probe technique. The pressure was always increased at room temperature, and at each pressure step the sample resistance was measured over the whole temperature range for the full cooling and heating cycle. The pressure was determined from the superconducting transition temperature of the Pb foil using the calibration table of Bireckoven and Wittig.[8] Two samples of NpSb were measured although one cell failed to reach pressures above 3 GPa, and was probably not in very hydrostatic conditions, due to a misalignment of the sintered diamond anvils.

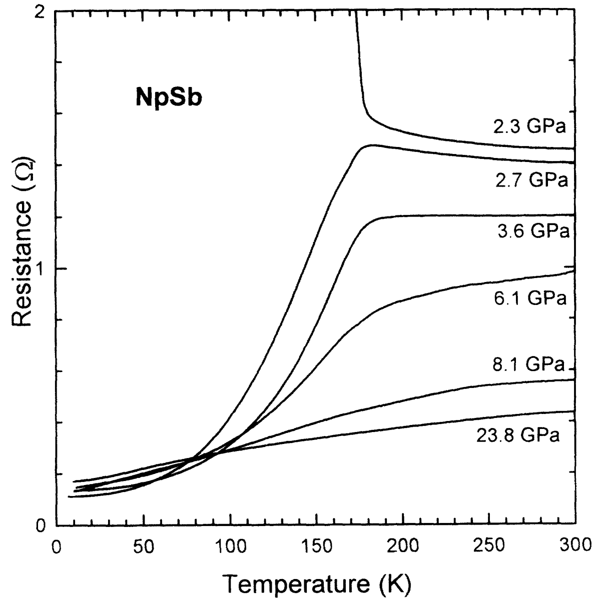

FIG. 2. Resistance vs pressure curves of NpSb at selected pressures from 2.3 to 23 GPa.

III. RESULTS

Figure 1 shows a selection of resistance versus temperature curves of NpSb for pressures up to 2.3 GPa. The normal pressure resistivity curve from Pleska[3] is shown as an inset. The curve measured at the lowest pressure (0.7 GPa) agrees well with the previous measurement for the high-temperature part where the resistivity exhibits a Kondo-like increase with decreasing temperature. The sharp increase in the resistance below T_N is also well reproduced. On the other hand, whereas the normal pressure measurement showed an almost temperature-independent resistivity below T_N with some oscillations, and with a ratio of the low-temperature resistance to the room-temperature value, $R(4.2\ \mathrm{K})/R(300\ \mathrm{K})$, of about 3–4, at the lowest pressure we find a pronounced semiconductorlike behavior, also with some oscillation. This different behavior is even more surprising as one of the main effects of applying pressure is to very quickly suppress this low-temperature resistance as can be seen in the successive curves upon increasing pressure. This result was confirmed qualitatively on both samples, which exhibited a ratio $R(4.2\ \mathrm{K})/R(300\ \mathrm{K})$ of about 30 in the case shown here, and a huge 1000 in the other case. Because of this discrepancy, another crystal, from the same batch as the second sample, was very recently measured at ambient pressure. At low temperature the resistivity was also found to increase even more strongly and a ratio $R(4.2\ \mathrm{K})/R(300\ \mathrm{K})$ of more than 10 000 was found.[9] The reasons for these different results are not understood. Slight variations of stoichiometry from one sample to another are a likely possibility. However, in spite of this difficulty the essential result appears to be that NpSb exhibits a semimetallic or semiconductorlike resistivity at low temperature which tends to be suppressed by the application of pressure.

The other effects which can be clearly seen in the low-pressure curves of Fig. 1 are the decrease of T_N with increasing pressure and a slight reduction in the high-temperature resistivity. Figure 2 shows the resistance versus temperature curves at pressures from 2.3 to 23.8 GPa. Between two successive pressure steps at 2.3 and 2.7 GPa, the behavior has changed quite dramatically, the presumed magnetic ordering now appears as a sharp decrease in the resistance while the behavior above the ordering temperature has changed very little. Further increasing the pressure leads to an obvious decrease in the high-temperature resistivity, a general rounding of the features of the curve, and a progressive trend from the high-temperature Kondo-like resistivity to a typical metallic behavior.

The ordering temperature can usefully be extracted from the resistance versus temperature curve from the maximum in the derivative dR/dT. This has been plotted for the two sets of curves in Figs. 3 and 4. For the first set T_N appears as a sharp negative peak. Close examination of the 2.7 GPa curve in the second set reveals a double discontinuity in the resistance. This appears as a double peak in the derivative which disappears (or the two effects are superimposed) in the subsequent pressure steps, to reappear at 6.1 GPa. These various features are plotted as a function of pressure in Fig. 5. Above about 8 GPa very little change is observed over the whole temperature range and the signature of magnetic ordering in the derivative completely disappears.

IV. DISCUSSION

A. The structural phase transition

X-ray-diffraction measurements at room temperature indicate a sluggish transition from the NaCl ($B1$) structure to a distorted CsCl (tetragonal) structure starting at 10 GPa and being complete at around 18 GPa. Upon

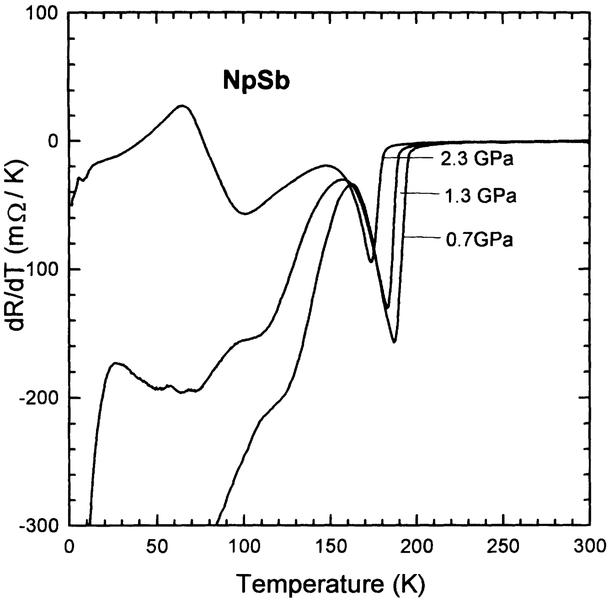

FIG. 3. The first derivative dR/dT for curves in Fig. 1 at pressures up to 2.3 GPa. The sharp negative peak corresponds to the Néel temperature, i.e., the onset of the triple-**k** antiferromagnetic order.

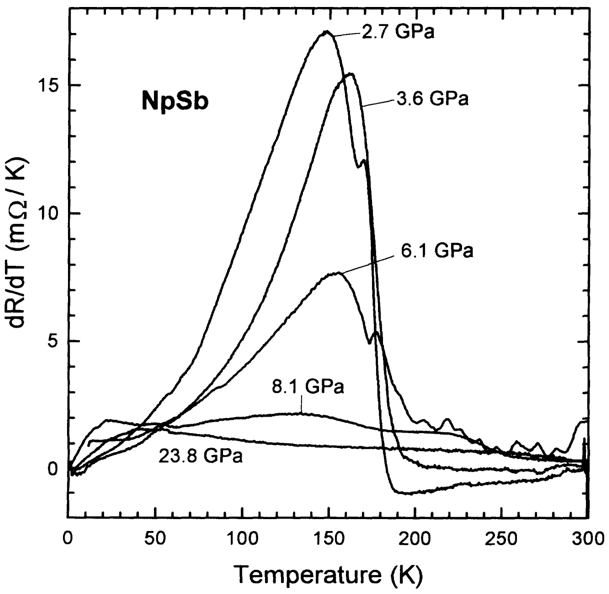

FIG. 4. The first derivative dR/dT for curves in Fig. 2 at pressures from 2.7 to 23 GPa. Please note the double peak in the 2.7 and 6.1 GPa curves.

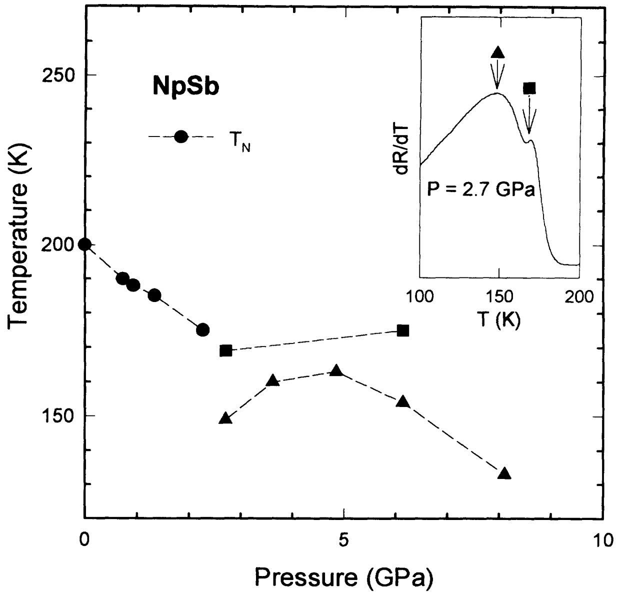

FIG. 5. Variation of the Néel temperature and other anomalies in the dR/dT curves vs pressure. Circles represent the Néel temperature as determined in analogy to the ambient pressure measurement. The inset shows the derivative dR/dT for $P=2.7$ GPa and explains the significance of the other symbols. Lines are just a guide to the eye.

releasing pressure a large hysteresis was found as the low-pressure phase was only fully recovered at 2 GPa.[4] As the authors point out, the relation between this structural transition and the delocalization of the $5f$ electrons is not clear. In the actinide metals the participation of the $5f$ electrons in the crystal bonding is thought to be responsible for the observed phase transitions to lower symmetry structures, accompanied by large volume collapses. The analogy with the NaCl compounds is, however, not simple, as this transition to the CsCl or similar structure occurs in many compounds, including some with no f electrons. It is, however, clear that if the volume collapse reduces the An-An spacing sufficiently, delocation of the $5f$ electrons will occur as a consequence of the structural transition.

In NpSb the Np-Np spacing in the high-pressure phase is apparently just above the limit of the Hill transition zone and there is some doubt as to whether delocalization of the $5f$ electrons occurs. If it is the case, some signature in the resistivity would certainly be expected. In Fig. 6 the isothermal resistances are shown versus pressure for room temperature and 4.2 K. The change in behavior between the two types of curves can be seen by the dramatic decrease in the 4.2-K resistance. One natural assumption might be to attribute this to the structural phase transition. However, we believe that this is not the case as the pressure is far too low compared with the x-ray results and there is no signature in the room-temperature resistance. On the other hand, there is a pronounced decrease in the room-temperature resistivity between 5 and 8 GPa which we suggest corresponds to the structural phase transition.

Of course the transition pressure at low temperature could be lower than at room temperature. However, if this were the case it would mean that upon cooling and warming we would cross and recross the phase boundary. As no hysteresis is seen between the cooling and warming curves, this is extremely improbable. In addition, there is a small but significant maximum in the low-temperature resistance at 6 GPa which could be due to an increase of disorder due to the coexistence of the two phases during the transition. On releasing the pressure, the high-temperature resistance remains almost constant down to the lowest pressures where it abruptly increases to ap-

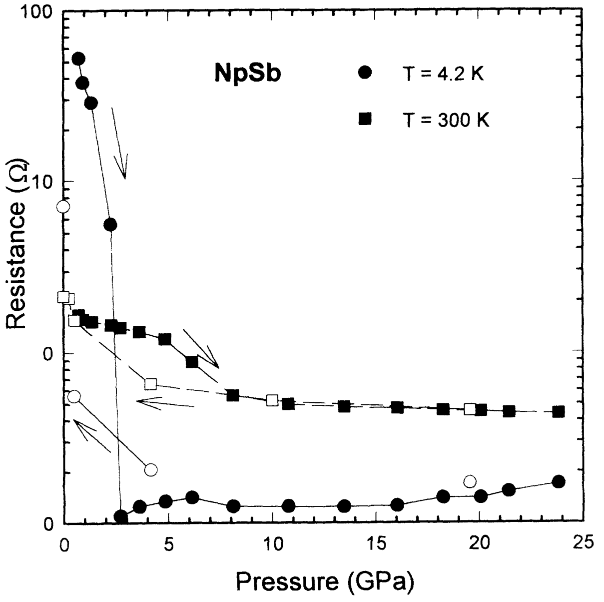

FIG. 6. The resistance of NpSb vs pressure at $T=300$ K (squares) and $T=4.2$ K (circles). Solid and open symbols represent increasing and releasing pressure, respectively.

proximately the initial value. This hysteresis is similar to that seen by x-ray diffraction.

This double signature of the phase transition, i.e., decrease in the high-temperature resistance and maximum in the low-temperature resistance, is remarkably similar to that found for PuSb.[6] The value of 5–8 GPa for the structural phase transition is still well below the value of 10–18 GPa found from x rays. This discrepancy seems now to be fairly systematic in the NaCl compounds and is also comparable to that found for PuSb. This difference in transition pressures is probably due to the different techniques used. This transition is generally very sluggish and exhibits strong hysteresis. It is therefore difficult to establish a true transition pressure in the thermodynamic sense. It is possible that when the tetragonal phase started to appear at 10 GPa in the x-ray experiment the $B1$ phase had been metastable for some time. The x-ray experiment is done in a diamond anvil cell with silicon oil as the pressure medium which, at least to 10 GPa is almost hydrostatic. In contrast it is possible that in the resistance measurement where the pressure medium is solid, the less hydrostatic and less homogeneous conditions tend to promote the phase transition at lower pressures. Finally we can remark that above 8 GPa there is very little change in the resistance curves over the whole temperature range. It is therefore unlikely that above this pressure any transition occurs.

These results do not provide direct evidence for or against the delocalization of the $5f$ electrons. However, the strong decrease in the room temperature resistance of almost a factor 3, and the apparent absence of any sign of magnetic ordering at pressures above 8 GPa both tend to suggest that despite the Np-Np spacing greater than the Hill limit, delocalization of the $5f$ electrons does occur at the structural phase transition to the tetragonal structure. Finally the extreme similarity of these effects to PuSb,[6] where delocalization was more expected, is another argument.

B. The variation of the Néel temperature

In analogy with the normal pressure resistance measurement, from 0 to 2.3 GPa the Néel temperature can be obtained quite accurately from the sharp increase in the resistance (Fig. 1) or the negative peak in the derivative (Fig. 2). T_N decreases linearly from the start with a slope of -11.5 K/GPa or a relative volume dependence of $d\ln T_N/d\ln V=3.1$. The different elements which enter into any calculation of the ordering temperature are the exchange integral J, the conduction-band susceptibility χ, and the spin S. In the case of rare earths, the spin of the localized $4f$ electrons is insensitive to pressure and the variation of the ordering temperature with pressure occurs through the change of J, which should increase with pressure, and χ, on which the effect of pressure is not really known.

In the case of actinides, where the $5f$ electrons are less localized, the situation is more complicated. There is almost certainly a direct effect of pressure on the spin. In addition if any Kondo screening of the moment is present, this is also likely to be very sensitive to pressure as pointed out by Fournier.[10] Doniach[11] showed that, with increasing exchange J (with pressure for example) in a one-dimensional Kondo lattice, the competition between Ruderman-Kittel-Kasuya-Yosida (RKKY) and Kondo interactions will lead to first an increase followed by a decrease of the ordering temperature. In a very recent review, Thompson and Lawrence[12] show that this picture describes the pressure dependence of magnetism in some Ce- and Yb-based compounds. As the authors point out, the lack of other high-pressure studies, and notably any information on the pressure dependence of the ordered moment, means that it is only speculative to apply this picture to U-based magnets, and this is also true for Np compounds. If NpSb does follow the behavior expected for competing RKKY and Kondo interactions, it would mean that at ambient pressure NpSb is already on the high-J side of the Doniach phase diagram and therefore further increasing the pressure leads to a monotonic decrease of T_N. However, at ambient pressure a moment of about $2.5\mu_B$ was measured,[2] which is close to the maximum for the trivalent Np ion and implies that no significant screening is present. This, together with the absence of any particular change with pressure in the resistivity above T_N, and certainly no increase in the slight Kondo-like behavior observed, are arguments against this explanation.

Another point to consider in the case of semimetals like NpSb is the possibility that the p-f mixing will play an important role. This hybridization of the f electrons with holes in the p band was described by Takahashi and Kasuya,[13] who showed that the effective f level is modified. The change in the effective f level is likely to be sensitive to pressure and this process was suggested to explain the variation of T_N with pressure in CeSb.[14] However, it seems that the effect of pressure is to increase the p-f mixing, leading in CeSb to a strong increase of

T_N, which is the opposite to the effect seen in NpSb.

On the other hand, it seems likely that in NpSb the direct effect of pressure on the spin will have a significant contribution to the variation of the ordering temperature. The value of $d \ln T_N / d \ln V = 3.1$ can be compared with the value for NpAs of 1.2 found from high-pressure Mössbauer spectroscopy[15] where the ordered moment was also found to decrease with pressure. This correlation of the variation of the magnetic moment and the ordering temperature was shown to hold for several other Np compounds exhibiting positive or negative values of dT_N/dP and at least partially supports this explanation. From the value of $d \ln T_N / d \ln V = 1.2$ Potzel *et al.*[15] deduce that NpAs is situated somewhere between the itinerant materials, which tend to exhibit a negative-pressure dependence of the ordering temperature, and the localized materials which can have a positive effect. NpSb would therefore, quite surprisingly, be even more itinerant than NpAs, in spite of the greater Np-Np spacing. In any case more information, mainly a measurement of the ordered moment under pressure, is undoubtedly necessary to resolve this question.

C. Magnetic ordering at high pressure

The most remarkable feature is the dramatic change in the behavior of the low-temperature resistance between 2.3 and 2.7 GPa. At ambient pressure the p^3 configuration of the pnictogen Sb requires all three electrons from the trivalent actinide ion Np^{3+} to fill the p band and NpSb is a semimetal. The increase in the resistance below T_N has been attributed to a gap opening at the Fermi level, or at least a strong decrease in the number of carriers in the X pocket of the Brillouin zone, due to the onset of this particular AF triple-**k** magnetic structure which seems to be most effective.[3] At 2.7 GPa this increase is replaced by a sharp decrease of the resistivity, which almost certainly also corresponds to the onset of magnetic ordering.

Two possible explanations for the sudden change in the temperature dependence of the resistivity are plausible. This change could be due simply to electronic changes to a more metallic band structure where the gap opening no longer occurs. It could also be due to a change in the nature of the magnetic structure to a less effective one. The absence of any marked change in the high-temperature resistivity might be evidence for the second case. In this context Mössbauer spectroscopy results under pressure[15] in NpAs implied, at about 5.5 GPa, a structural transition to a tetragonal phase, with a c/a ratio sufficiently close to 1 to be invisible to x rays, but with very different magnetic properties. Two subspectra were also seen at this pressure and this, together with the fact that the volume of the low-temperature triple-**k** phase of NpAs is greater than that of the high-temperature single-k phase, suggests that pressure may push NpAs into a single-k phase. It is possible that a similar effect is present in NpSb and could be responsible for the change in the resistivity. The double peak in the derivative might also be the signature of a double transition, though we emphasize that this is pure speculation at this point.

The radical change in the resistance versus temperature behavior makes a direct comparison of the ordering temperature with that of the lower-pressure curves difficult. However, if we suppose that the sharp drop in resistance below approximately 170 K is due to the onset of magnetic order, a significant temperature, T_0 can be obtained from the positive peak in the derivative, which in two cases (2.7 and 6.1 GPa) appears to be a double peak. Taking the main peak, the variation of T_0 versus pressure shows a marked discontinuity between 2.3 and 2.7 GPa, where the change in behavior occurs. This may or may not be significant as the change from a negative to a positive slope in the resistance versus temperature curve may influence the result obtained from this method used to determine the transition temperature. On the other hand, there is also a discontinuity in the slope of the T_0 versus pressure behavior above 2.7 GPa, where T_0 increases, going through a maximum at about 5 GPa and then decreasing. The secondary peak appears at a temperature which is comparable to T_N at the previous pressure, and apparently shows no marked change with pressure between 2.7 and 6.1 GPa. This peak does not appear in the derivative for the intermediate pressure steps, though it may well be masked by the increase in temperature of the main peak.

The Kondo-like behavior in the high-temperature resistivity which was rather constant up to about 3 GPa, progressively disappears at higher pressures. Above 8 GPa the resistance versus temperature curves hardly change with pressure and are of a nearly metallic nature. No marked singularities are present in the derivative which suggests, as already mentioned, that the high-pressure phase is nonmagnetic, though only a direct measurement could confirm this.

V. CONCLUSION

This high-pressure resistance study of NpSb up to 23 GPa shows at the same time the possibilities and the limits of this technique. The structural transition to the tetragonal phase is found to occur around 6 GPa and the high-pressure phase is likely to be nonmagnetic. We suggest that this transition is associated with the delocalization of the $5f$ electrons. At low pressure the Néel temperature is found to decrease with pressure at a rate of about -11.5 K/GPa. We suggest that the direct effect of pressure on the spin may play a significant part in this variation although more information is needed to confirm this. At a pressure between 2.3 and 2.7 GPa a dramatic change in the resistance versus temperature behavior indicates some marked electronic or magnetic transformation in NpSb. We speculate that the second possibility is more likely though once again further measurements are necessary. The relatively low pressure at which this change occurs should be accessible to other techniques such as magnetic susceptibility or even neutron scattering to resolve this question though these techniques are as yet not accessible for transuranium compounds. In the immediate future a Mössbauer spectroscopy under pressure experiment is planned which may elucidate some of these points. In any case these results show that the high-pressure properties of NpSb are more complex than might originally have been imagined, and NpSb is a rich potential candidate for other high-pressure studies.

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