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Superconducting and Normal State Properties of Barium Tantalum Sulfide

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Two types of compound in $BaTa_2S_5$ were specified according to their physical properties and superlattice arrangements. Electrical resistivity and ac magnetic susceptibility measurements indicate that both compounds are superconducting with transition temperatures $T_c = 2.88$ or 3.14 K, respectively, being dependent on formation processes of the specimens. The normal state properties, such as resistivity, Hall coefficient, magnetoresistance, and magnetic susceptibility, are also different between the two types of compound. Especially, magnetic susceptibility for the one type with lower T_c shows a Curie–Weiss-type paramagnetism below about 50 K, while that with higher T_c shows a temperature independent paramagnetism with a clear cusp at 70 K. Electron diffraction experiments show that the superlattice of the former compound is $a\sqrt{28} \times a\sqrt{28} \times nc$, while the structure of the latter consists of two types of superlattice which stack alternatively along the c axis. © 1995 Academic Press, Inc.

INTRODUCTION

The compound $BaTa_2S_5$, which was found in our laboratory (1), is superconducting below about 3 K but details of the properties have not been reported thus far (2). The crystal structure has not been determined because of a complicated structure with a large superlattice. The sublattice is hexagonal with $a = 3.326$ Å and $c = 25.21$ Å. The unit size of the superlattice is $a\sqrt{28} \times a\sqrt{28} \times nc$, where n stands for an unknown number probably somewhere between 10 and 20 (1).

This paper reports the superconducting and normal state properties of $BaTa_2S_5$. Two types of superconducting properties were observed for specimens which were prepared by different heat treatments. These specimens exhibited pronounced differences of electrical and magnetic properties in their normal states. The crystal structures of these specimens were investigated by X ray and electron diffraction methods.

EXPERIMENTAL

The synthesis of $BaTa_2S_5$ has been reported in a previous work (1). In the present study, some specimens with different lattice parameters and crystallinities were prepared. The starting materials, $BaCO_3$ and Ta_2O_5, were mixed in the proportion of Ba/(Ba + Ta) = 0.33. Three manners of the sulfurization of the mixture were tried: (a) the mixture was kept at 700°C for 1 day and 900°C for 3 days in an atmosphere of CS_2 carried by N_2 gas, followed by cooling in steps 100°C/min (specimen A). (b) The mixture was kept at 750°C for 3 days in the same atmosphere as (a) and was again heated at 900°C in an evacuated silica tube for 3 days, followed by quenching into water (specimen B). (c) The mixture was kept at temperatures of 600, 700, and 900°C for 1 day in the same atmosphere as (a) and was again heated at 900°C for 3 days in an evacuated silica tube, followed by cooling slowly to room temperature overnight (specimen C).

X ray powder diffraction patterns of these specimens were obtained by an X ray diffractometer using Cu$K\alpha$ radiation. The 100 and 110 reflections of $BaTaS_3$ were weakly seen in the pattern of specimen A and very weakly in B and C. For A, an unknown peak at $2\theta = 31.9°$ was also observed. The preferred orientation of 001 for the specimen was estimated by ε-scanning method (3). Electron diffraction measurements were made by an electron microscope (Hitachi Co., H-500). A few contaminants of $BaTaS_3$ and TaS_2 were observed in the measurement of specimen A. The sulfur content of $BaTa_2S_5$ was gravimetrically analyzed by measuring the change in weight between the mixture of the starting materials and the sulfurized product. It has been confirmed by a previous chemical analysis that Ba and Ta elements do not evaporate from a specimen in preparation (1).

Electrical resistivity, magnetoresistance, and Hall coefficient measurements were made by standard direct current four-probe methods. For the measurements, thin rectangular plates (about 0.2 mm in thickness, 8 ~ 10 mm in length, and 1.5 ~ 2 mm in width) were prepared by compressing and sintering powders of A and C in evacuated silica tubes at 950 and 900°C for 3 days, respectively. The temperature of the electrical experiment was measured in a temperature range between 1.6 and 300 K by a calibrated carbon-glass sensor (LakeShore Cryotronics,

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Inc., CGR-1-1000). Superconducting diamagnetization measurements below 4.2 K were made by an alternate current (ac) susceptibility method using an LCR meter (Kokuyo Co., KC-535C) and a calibrated Ge temperature sensor (LakeShore Cryotronics, Inc., GR-200A-500), where Pb powder was used as a standard sample (Rare Metallic Co., 99.999% in purity, 100–200 mesh).

Magnetic susceptibility measurements in the normal states were performed on a SQUID magnetometer (Quantum Design Co., MPMS HP-150) at an applied field strength 10.0 kOe and also made by a Faraday type magnetometer at 10.2 kOe. The susceptibility of a copper rod (99.999% in purity) was measured at 200 K for the calibration of the SQUID magnetometer. For the calibration of the Faraday type magnetometer, the susceptibilities of Au and Si were measured at 293 K and excellently agreed with previous data (4).

The magnetic susceptibility of $BaTa_2S_5$ was already reported in a temperature range between 77 and 273 K, which was measured by the Faraday type magnetometer (1). The susceptibility measured previously was larger in one order magnitude than that obtained in the present experiment. It was found after publishing the previous paper (1) that a slight flux leakage from an applied magnetic field had an influence on the operation of an electric balance and generated a systematic error for a very weak susceptibility such as that of $BaTa_2S_5$. The absolute magnitude of the previous susceptibility is therefore necessary to be corrected in the present paper, as described later.

RESULTS

Superconducting Properties

The resistivity of specimen A begins to drop at about 3.3 K and becomes zero below 3.07 K within an experimental precision ±0.02 K, while that of C begins to decrease at about 3.0 K and becomes zero at 2.82 K, as shown in Fig. 1. The superconducting transition temperature (T_c) for A was assigned to be 3.14 K, where the magnitude of resistivity was half of the resistivity in the normal state and that for C was 2.88 K. The magnitude of resistivity of C in the normal state is about three times larger than that of A.

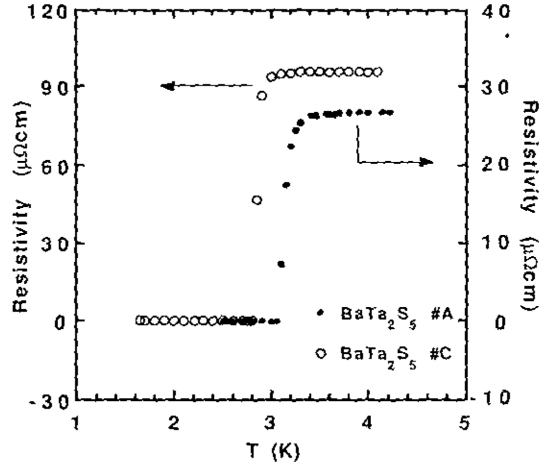

FIG. 1. Superconducting transition in resistivity for $BaTa_2S_5$.

The temperature dependence of ac susceptibilities of specimens A and C are shown in Fig. 2, where the susceptibility of Pb is also shown for reference. The temperature dependence of susceptibility of B is almost the same as that of C and is not shown in the figure for clarity. The superconducting diamagnetic deviation of A again starts at 3.08 K, while that of C starts at 2.82 K. The superconducting volume ratios of A and C are estimated to be about 65 and 38% at 1.5 K, respectively, assuming an ideal superconducting magnetization for the Pb sample. The volume ratio of B is the same as that of C.

Normal State Properties

Both electrical resistivities of specimens A and C are metallic (Fig. 3). The latter at 297 K is 1.1×10^3 μΩ cm which is 1.7 times larger than the former. The ratio between resistivity at 5 K and that at 297 K is 23 for A and 12 for C, respectively. Thus, the residual resistivity of C is 3.3 times larger than that of A. The temperature derivative of resistivity for A increases little around 70 K by 13% with increasing temperature.

Both Hall coefficients of A and C are positive in a whole temperature range (Fig. 4). The Hall coefficient of A pronouncedly increases below about 70K upon cooling. Around that temperature, a small peak is observed, as shown by an arrow in the figure. On the other hand, the

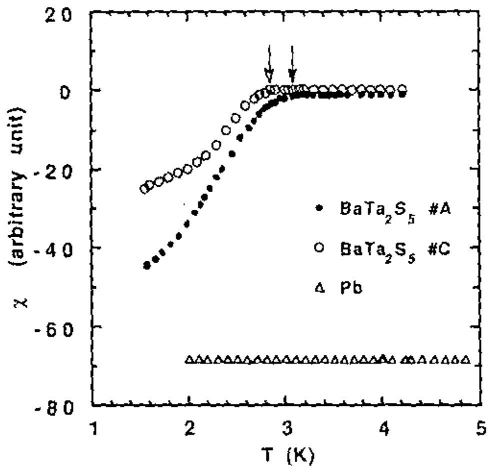

FIG. 2. Superconducting transition in ac magnetic susceptibility for $BaTa_2S_5$.

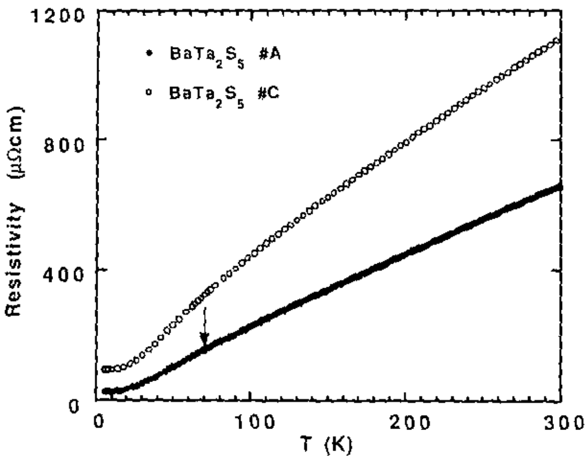

FIG. 3. Electrical resistivity of $BaTa_2S_5$ in the normal state. The temperature derivative of resistivity for A changes slightly at the temperature marked by an arrow.

Hall coefficient of C increases below about 70 K less than that of A and no peak such as that seen for A is observed around 70 K, although the Hall coefficient of C is rather scattered in the temperature range between 100 and 180 K. It is probably due to some experimental disturbances such as the occurrence of Joule heat because of its relatively high resistivity. The carrier densities of A and C at room temperature are 3.9×10^{21} (0.93/sublattice) and 6.4×10^{21} cm^{-3} (1.5/sublattice), respectively, assuming a single band for the conduction of each specimen. The Hall mobilities of A and C at this temperature are 2.4 and 0.9 cm^2 V^{-1} sec^{-1}, respectively.

The magnetoresistance of A and C at 5 K are shown in Fig. 5. The magnitude of the former at 9.5 kOe, 10%, is 5.3 times larger than that of the latter. Both magnetoresistances increase linearly with magnetic field strength.

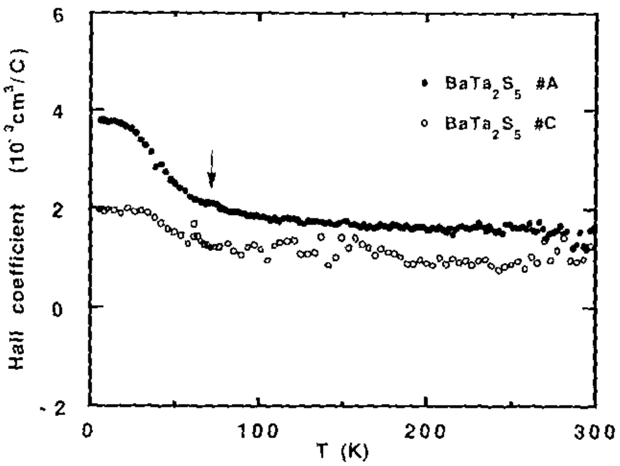

FIG. 4. Hall coefficient of $BaTa_2S_5$ in the normal state. A small peak is seen at the temperature marked by an arrow.

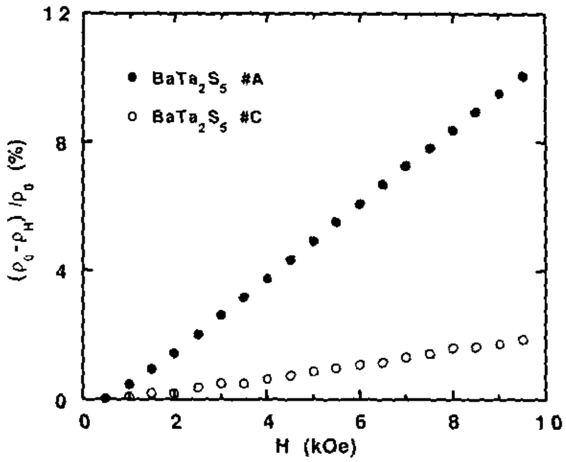

FIG. 5. Field dependence of magnetoresistance for $BaTa_2S_5$ at 5 K.

The large magnetoresistance of A observed at 5 K rapidly decreased with increasing temperature and became 2% at 30 K.

Magnetic susceptibilities of specimens A and C measured by the SQUID magnetometer are intrinsically Pauli paramagnetic above about 100 K and the latter is about 2 times larger than the former (Fig. 6). The magnitude of susceptibility of C at 293 K measured by the Faraday type magnetometer was 0.69×10^{-7} emu/g which excellently agreed with that obtained by the SQUID method. The susceptibilities of both specimens below about 100 K, however, are very different to each other. The susceptibility of C is paramagnetic which obeys the Curie–Weiss law very well and is described as $\chi_g = \chi_0 + C/(T - \theta)$, where $\chi_0 = 0.604 \times 10^{-7}$ emu/g, $C = 14.72 \times 10^{-7}$ Kemu/g, and $\theta = 3.85$ K. The Curie constant C gives an average effective moment at most 0.06 μ_B/Ta; i.e., the density of paramagnetic tantalum ions which could have a spin with

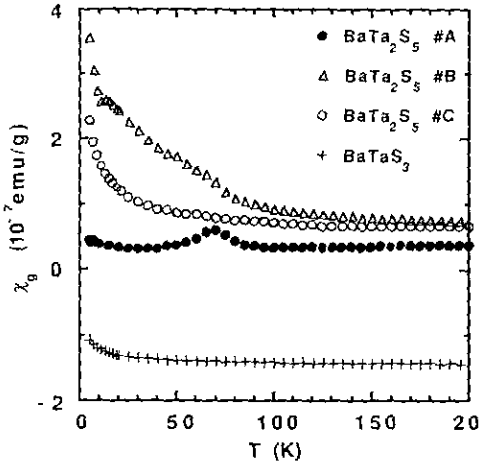

FIG. 6. Magnetic susceptibility of $BaTa_2S_5$ in the normal state measured under 10 kOe. The susceptibility of $BaTaS_3$ is also shown.

$S = 1/2$ is 0.1%. The susceptibility of B also shows a Curie–Weiss-like paramagnetism at low temperatures, although a very broad peak slightly overlaps the paramagnetic susceptibility from about 80 to about 20 K. The broad peak is probably due to the susceptibility of oxygen. In contrast with the susceptibilities of C and B, the susceptibility of A has almost no paramagnetic tail at low temperatures. Further, a clear cusp is seen at 70 K. Around this temperature, the resistivity and Hall coefficient of A weakly change, as mentioned above. The susceptibility of $BaTaS_3$ which is a contaminant phase included slightly in the present specimens was diamagnetic with $\chi = -1.9 \times 10^{-7}$ emu/g at 273 K and was almost independent of temperature in the temperature range measured (Fig. 6).

Characterization of Specimens

The X ray patterns of $BaTa_2S_5$ specimens systematically changed upon going from C to A via B. Reflections in the pattern of C (Fig. 7) had excellent sharp profiles, as seen in the pronounced splitting of $CuK\alpha_1$ and $CuK\alpha_2$ reflections between $2\theta = 35°$ and $60°$. The strong intensities of 00*l* reflections suggested the preferred orientation of [00*l*] for specimen C. This was really confirmed by the ε-scanning method. The indexing in the figure was made on the basis of a hexagonal subcell with $a = 3.3258(5)$ Å and $c = 25.208(4)$ Å which agreed well with previous values (1). In contrast with the pattern of C, reflections in the pattern of A were rather broad and the splitting of $CuK\alpha_1$ and $CuK\alpha_2$ reflections was hardly observed below $2\theta = 60°$ (Fig. 7). It is noted in the pattern of A that the intensities of 1, 0, $2m + 1$ ($m = 0 \sim 5$) are very weak but 1, 0, $2m$ ($m = 1 \sim 6$) are not so. The intensities of 00*l* are very low in comparison with those of C. The ε-scanning method showed that specimen A on X ray diffractometry was randomly orientated. The lattice parameters of A were $a = 3.3204(5)$ Å and $c = 25.005(4)$ Å which were smaller than those of C. In the case of specimen B, the splitting of $CuK\alpha_1$ and $CuK\alpha_2$ reflections as well as the intensities of 1, 0, $2m + 1$ and 001 were intermediate between those of C and A. The lattice parameters of B were $a = 3.3203(5)$ Å and $c = 25.083(4)$ Å which were almost the same as those of A.

The electron diffraction patterns of a^*–b^* and c^*–a^* for specimen C are shown in Figs. 8a and 8b, respectively, which are similar to those in the previous report (1). Superlattice reflections in the a^*–b^* pattern form a hexagonal net, $(\mathbf{a}^* + 2\mathbf{b}^*)/14 \times (-2\mathbf{a}^* + 3\mathbf{b}^*)/14$. Superlattice reflections in the c^*–a^* plane run along the c^* axis and are $i/2, 0, j/n$, where i is an odd number and n cannot be decided because of the difficulty in counting the number of weak spots in the rows. Both patterns are thus indexed with a hexagonal superlattice $a\sqrt{28} \times a\sqrt{28} \times nc$. On the other hand, the a^*–b^* and c^*–a^* patterns of specimen A are pronouncedly different from those of C (Figs. 8c and 8d): the a^*–b^* pattern consist of two types of superlattice reflections which show almost equal reflection intensities. One type of superlattice reflection is the same hexagonal net mentioned above. Another type is a hexagonal net $(2\mathbf{a}^* + \mathbf{b}^*)/14 \times (-\mathbf{a}^* + 3\mathbf{b})/14$ which agrees with a pattern generated by rotational operation of the first type with the angle between [120] and [210], i.e., 21.8°. This superlattice reflection type was also observed very weakly for speci-

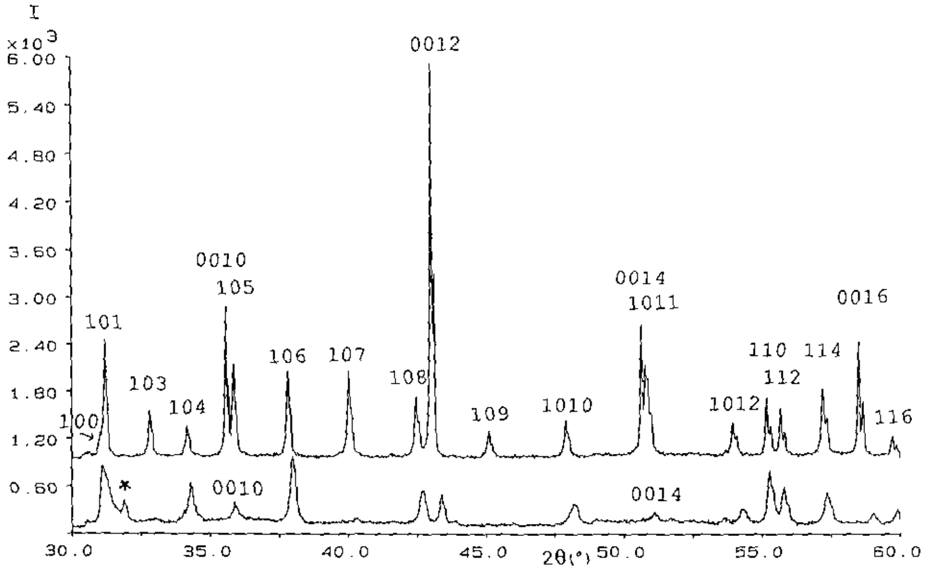

FIG. 7. X ray powder diffraction patterns of $BaTa_2S_5$. The upper pattern is for C and the lower is for A. The peak marked by * in the lower pattern is an unknown peak.

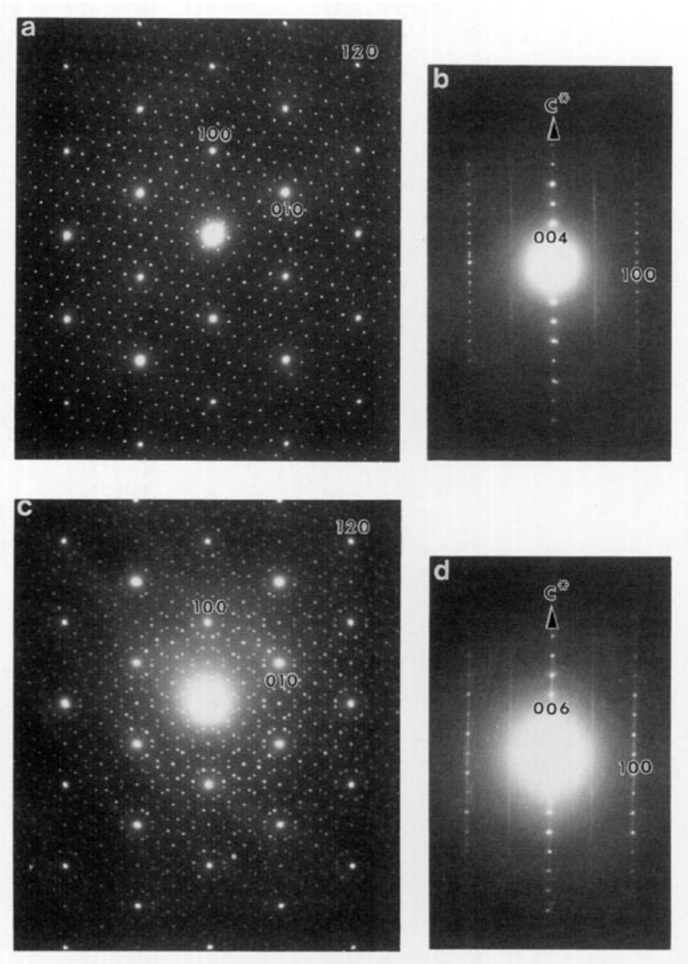

FIG. 8. Electron diffraction patterns of $BaTa_2S_5$: (a) a^*–b^* pattern of C, (b) c^*–a^* pattern of C, (c) a^*–b^* pattern of A, and (d) c^*–a^* pattern of A.

TABLE 1

Comparison of Sublattice Parameters, Superlattice Reflections, Superconducting, and Normal State Properties

	Sublattice parameters		Superlattice reflections			
Specimen	a (Å)	c (Å)	S1	S2	T_c (K)	Volume ratio (%) at 1.5 K
A	3.3204(5)	25.005(4)	++	++	3.14	65
B	3.3203(5)	25.083(4)	—		2.88	38
C	3.3258(5)	25.208(4)	++	+−	2.88	38

Specimen	Resistivity at 5 K ($\mu\Omega$ cm)	Magnetoresistance at 9.5 kOe and 5 K (%)	Hall coefficient at 5 K (10^{-3} cm^3/C)	Magnetic susceptibility at 5 K (10^{-7} emu/g)
A	28	10	3.8	0.4, Pauli para
B	—	—	—	3.8, C.W. para
C	96	1.9	2.0	2.3, C.W. para

Note. S1 represents the superlattice reflection $(\mathbf{a}^* + 2\mathbf{b}^*)/14 \times (-2\mathbf{a}^* + 3\mathbf{b})/14$ and S2 the reflection $(2\mathbf{a}^* + \mathbf{b}^*)/14 \times (-\mathbf{a}^* + 3\mathbf{b}^*)/14$. The marks "++" and "+−" imply "dominant" and "scarce," respectively. The mark "—" represents "no measurements."

men C. In addition to these superlattice reflections, other very weak superlattice reflections are also observed for specimen A. They form a hexagonal net of reflections $\mathbf{a}^*/14 \times \mathbf{b}^*/14$ and thus correspond to a hexagonal superlattice $14\mathbf{a} \times 14\mathbf{b}$.

The c^*–a^* pattern of specimen A is also different from that of C. For the case of A, the fundamental reflections $1, 0, 2m + 1$ are very diffuse or split along c^* in contrast with the sharpness of $1, 0, 2m$ (Fig. 8d), which agrees with the results of X ray diffractometry for A. For the case of C, both reflections of $1, 0, 2m + 1$ and $1, 0, 2m$ are not diffuse. Superlattice reflections, $i/2, 0, j/n$, in the c^*–a^* plane of A appear to be similar to those of C.

The gravimetric analysis showed that the sulfur content of specimen C was 24.0 wt% which was 0.05 wt% larger than that of A, i.e., the compositions of C and A were $BaTa_2S_{4.914}$ and $BaTa_2S_{4.903}$, respectively. The analysis suggests that specimen A is more sulfur deficient than C, but the difference of sulfur content is very small.

The present experimental results mentioned thus far are evidently dependent on the specimens. Several differences between the sublattice parameters, superlattice reflections, and physical properties of the specimens are summarized in Table 1.

DISCUSSION

The results of resistivity and susceptibility below 4.2 K indicate that $BaTa_2S_5$ is a bulk superconductor and its superconducting properties are dependent on the formation processes of specimens. The superconducting transition temperature of specimen A is about 10% higher than that of C and the superconducting volume ratio of the former is about two times larger than that of the latter. These properties of B are the same as those of C. The crystal quality of C is however superior to that of A, judging from the X ray diffraction experiments.

On the other hand, the sublattice dimensions, especially c, of A are smaller than those of C but almost the same as those of B. The smaller dimensions suggest that specimens A and B are sulfur deficient, which is supported by the gravimetric analysis. Previous chemical analysis of the compound, however, gave an ±0.1 wt% error in sulfur content which was twice the present difference of sulfur content (1). The present gravimetric analysis was based on the assumption that metal species did not evaporate. Since the assumption is confirmed only within the accuracy of the chemical analysis reported previously and further specimen A includes slight other phases, the present analysis is not decisive from the viewpoint of experimental accuracy.

In contrast, specimens A and B which have almost the same lattice dimensions show different superconducting properties, and the specimes B and C which have evidently different lattice dimensions show almost the same superconducting properties. It is thus stated that the different superconducting properties of specimens A and C (B) are not ascribed to merely the difference of their lattice dimensions or the difference of their sulfur compositions.

The electron diffraction patterns of specimen C are quite similar to those reported previously and show that the superlattice is $a\sqrt{28} \times a\sqrt{28} \times nc$ (1). In contrast, the diffraction patterns of A indicate that two types of superlattices coexist in the equal volume ratio. One superlattice is the same as that of C in the c plane. Another superlattice has the same dimensions in the c plane but is at an angle of 21.8° with the former superlattice. These facts indicate that both superlattices stack alternatively along the c axis and the interval of stacking is in the order of the superlattice dimension along the c axis. It is noted that the $14\mathbf{a} \times 14\mathbf{b}$ net forms common superlattice points of both superlattices. Thus, the electron beam should really interact a periodic potential generated by the net, as long as these lattice points are in the coherent range of electron diffraction, even when they exist over some stacks of both superlattices. This results in the net pattern of $\mathbf{a}^*/14 \times \mathbf{b}^*/14$ observed. This net pattern could also be explained by the dynamical effect of electron diffraction, i.e., double reflections passing through the different types of superlattices, but it is much better to consider that the observed net pattern is evidence of the stacking manner of both superlattices, as mentioned above. It is probable that the stacking faults exist periodically in the case of A, as suggested in its lower residual resistivity.

The fundamental reflections of $1, 0, 2m + 1$ in the c^*–a^* pattern of electron diffraction for A are very diffuse or split along c^*, while those of $1, 0, 2m$ are sharp. The X ray diffraction pattern of A gave the same result. This means that the sublattice periodicity along the c axis is modified from the typical structure of $BaTa_2S_5$ which probably corresponds to the crystal structure of C. The modified periodicity may be correlated with the stacking manner of both superlattices. More detailed analysis of the crystal structure of the compound is a future problem.

Some physical properties of specimen A in its normal state differ much from those of C. Particularly, the difference of the magnetic susceptibilities of both specimens is very pronounced. The clear cusp of susceptibility for A is seen at 70 K, where the slight changes of the resistivity and the Hall coefficient are observed. This anomaly of susceptibility is an intrisic property of specimen A, because the susceptibilities of $BaTaS_3$ and TaS_2, i.e., contaminant phases, do not show such an anomaly at that temperature. The paramagnetic tail of susceptibilities of B and C observed at low temperatures was not ascribed to other magnetic elements or magnetic impurities, because such a tail was not observed for the susceptibilities of A and $BaTaS_3$ which were prepared by using the same reagents as those of C. Thus, the paramagnetic tail is probably an intrinsic property of specimen C. This is also seen in the susceptibility of B. In respect to the interpretation of the cusp, only specimen A does not seem antiferromagnetic below 70 K or to be in a spin glass state, because the susceptibilities of C and B show no indication of magnetic ordering far below 70 K. The meaning of the cusp is unknown at present. It should however be noted that paramagnetic local moments exist in C and B but do not in A. This difference about the existence of paramagnetic local moments is probably due to different degrees in the hybridization of conducting electrons and virtual bound states. It suggests some difference between the electronic structure of A and that of C (B).

The resistivity of C is higher than that of A. The residual resistivity of C is 3.3 times larger than that of A. This fact seems to be rather curious, because the crystal quality of C is superior to that of A, judging from the comparison of X ray patterns. Some reasons can be considered: (i) The incomplete sulfur arrangement may affect the residual resistivity of C, because the X ray diffraction patterns strongly reflect the arrangements of heavy barium and tantalum atoms but reflect less the arrangement of light sulfur. (ii) The stacking faults at the boundaries between the two types of superlattices mentioned above may periodically be arranged in the case of A. In the case of C, the stacking faults are far less but should randomly exist. The periodical stacking faults of A should result in its lower residual resistivity. In addition to these structural aspects, the scattering of paramagnetic local moments for the case of C may yet be responsible for its high residual resistivity to some degree. The contribution of phonon scattering in resistivity for C is also 1.6 times larger than that for A. The Brillouin zone and Fermi surface of A are reduced by the existence of 14**a** × 14**b** periodic potential, which may be resposible for the decrease of electron phonon scattering.

The magnetoresistance of A is large, while that of C is small. The magnetoresistance is on the order of magnitude of $(\omega_c\tau)^2$ (5), where ω_c and τ are the cyclotron frequency and relaxation time, respectively. The ratio between relaxation times of A and C is the ratio between their residual resistivities, assuming the same effective mass of conducting electrons for both specimens. A magnetoresistance ratio evaluated from the ratio between both squares of the residual resistivities is 11.6 and roughly agrees with the observed ratio 5.3, assuming that the cyclotron frequencies of both specimens are the same. The difference of magnitudes of magnetoresistance can thus be explained by the difference of relaxation times of both specimens. The Hall coefficients of A and C are positive, which suggests rather complicated electronic structures of both specimens. The temperature dependence of Hall coefficient of A largely varies at low temperatures. In contrast, that of C changes less. The compound $BaTa_2S_5$ has probably a layered structure. If so, anisotropic Fermi surface and anisotropic relaxation time may be expected. The longer the relaxation time at low temperatures the more strongly reflected the characteristics of Fermi surface. It is considered that the longer relaxation time and anisotropic Fermi surface of A are responsible for the large magnetoresistance and the large variation of Hall coefficient.

The difference of superconducting transition temperatures of the specimens may be explained through the difference of their electronic density states or their electron phonon interactions. Some difference in the electronic structures are really suggested by the magnetic susceptibility data. However, the difference of superconducting volume ratios may be correlated with the degree of imperfections and magnetic disturbances in the crystals rather than the electronic density states or the electron phonon interaction. The paramagnetic local moments of B and C certainly degrade their superconductivities in comparison with the superconductivity of A without paramagnetic local moments.

CONCLUSION

There are two types of compound in $BaTa_2S_5$ according to the varieties of superlattices and physical properties of both superconducting and normal states. Specimens B and C belong to one type (type 1 compound) and specimen A belongs to another (type 2 compound).

The superlattice of the type 1 compound is $a\sqrt{28} \times a\sqrt{28} \times nc$, while the crystal structure of the type 2 compound consists of alternate stacks of the two type superlattices.

The latter compound is superconducting below 3.14 K with a superconducting volume ratio 65% at 1.5 K, while the former compound is superconducting below 2.83 K with the ratio 38%. This difference is not necessarily ascribed to the variation of sublattice parameters of $BaTa_2S_5$.

The long relaxation time of the type 2 compound suggests some possibilities in respect to its crystal structure: (i) its sulfur arrangement is less incomplete than that of the type 1 compound or (ii) the alternate stack of the two types of superlattices is periodic along the *c* axis for the case of the type 2 compound.

The varieties of magnetoresistances and Hall coefficients of both compounds can be understood in terms of their different relaxation times.

The difference in respect to whether paramagnetic local moments exists or not suggests some difference in the electronic structures of both compounds.

It is possible that some difference in the electronic structures is responsible for the variety of superconducting properties. In addition to this, the existense of paramagnetic local moments for the type 1 compound certainly degrades their superconductivities in contrast with the superconductivity of the type 2 compound.

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