Enhanced magnetoresistance in the binary semimetal $NbAs_2$ due to improved crystal quality

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We have observed an extremely large magnetoresistance exceeding 1.9 million at 1.7 K at 40 T for a single crystal of the binary semimetal $NbAs_2$. The magnetoresistive behavior for this compound is quantitatively reproduced by a semiclassical two-carrier model in which the significant enhancement of magnetoresistance is attributed to the almost full compensation of the hole and electron densities ($0.994 < n_h/n_e \leqslant 0.999$) as well as the high mobility ($>6 \times 10^5$ cm^2/V · s). Our results indicate that binary semimetals with higher carrier densities have a great potential for exhibiting a further divergent increase in magnetoresistance merely through an improvement in crystal quality.

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I. INTRODUCTION

Magnetoresistance (MR) is a change in the electrical resistance in an external magnetic field, and is applied to a wide variety of instruments, such as magnetic heads and sensors. This is one of the most fundamental phenomena originating from the interplay between electricity and magnetism, and thus is regarded as a central research topic in material science. High mobility compensated semimetals and metals, in which the positive-charge carrier density is nearly equal to the negative one, are known to show large MR owing to their cancellation of the Hall voltage [1–5]. Elemental bismuth, graphite, and cadmium are known as the prototypical semimetals exhibiting a huge MR ($\rho(\mu_0 H)/\rho(0\mathrm{T})$) exceeding $10^4 \sim 10^6$ at 4 K at several tesla [6–11]. Recently, large MR values have been reported for a wide variety of binary semimetals, attracting the attention of researchers [12–23]. The MR for these materials reaches $10^3 \sim 10^5$ without an indication of saturation even at several tens of tesla, although even these large MR values are far smaller than those observed in elemental semimetals.

In general, electrical resistivity in a semimetal is explained by two carrier models, as follows [1]:

$$\rho_{xx} = \frac{1}{e}\frac{(n_e\mu_e + n_h\mu_h) + (n_e\mu_h + n_h\mu_e)\mu_e\mu_h(\mu_0 H)^2}{(n_e\mu_e + n_h\mu_h)^2 + (n_e - n_h)^2\mu_e^2\mu_h^2(\mu_0 H)^2}, \tag{1}$$

where μ_e,μ_h,n_e, and n_h denote electron mobility, hole mobility, electron density, and hole density, respectively. In Eq. (1), we note that the charge compensation term $(n_e - n_h)^2$ in the denominator is an important parameter for determining the saturation value of MR in a high-field limit. Namely, $\rho(\mu_0 H \to \infty)/\rho(0\ \mathrm{T})$ becomes infinite as $(\frac{n_e}{n_e - n_h})^2$ in the case of $n_e \approx n_h$. Despite the definition of semimetal ($n_e = n_h$), small differences between n_e and n_h are inevitable in real systems due to crystalline imperfections causing stoichiometric imbalance. To overcome this sensitivity to local stoichiometry, compensated semimetals with higher carrier densities would be advantageous to exhibit large MR by realizing a higher compensation ratio ($\frac{n_h}{n_e} \approx 1$). This can be achieved using recently reported binary semimetals [12–23]. Another important factor for large MR in a reachable magnetic field is carrier mobility μ. With higher mobility or a lower scattering rate of the charge carrier, a lower magnetic field can prevent a linear motion of the charge carrier along an applied electric field due to the Lorentz force when $\boldsymbol{E} \perp \boldsymbol{B}$. In fact, for ultrahigh mobility elemental semimetals such as bismuth, the MR tends to grow rapidly in only a few tesla, resulting in MR much larger than those recently reported for the binary systems. On the other hand, the binary semimetals are likely to have lower carrier mobility, as evidenced by their large residual resistivity in spite of their high carrier density. Thus, the increasing rate of MR is suppressed, resulting in a nonsaturating MR with a much smaller value in a reachable field. Therefore, it may be possible to enhance the MR in binary semimetals merely by improving the crystal quality.

In this paper, we report an unprecedentedly large MR exceeding 1.9×10^6 at 40 T at 1.7 K for a single crystal of $NbAs_2$. Our reported MR in $NbAs_2$ is several tens of times larger than those in the previously reported binary semimetals [12–23] and is comparable to those in ultrahigh mobility elemental systems [8–10]. The huge enhancement of the MR is attributed to not only the high carrier mobilities($\mu > 600{,}000$ cm^2/Vs) but also the almost full charge compensation ($0.994 < n_h/n_e \leqslant 0.999$ with $3 \times 10^{19} \leqslant n_e \leqslant 1.3 \times 10^{20}$ cm^{-3}) due to the improvement of crystal quality.

II. EXPERIMENT

Single crystals of $NbAs_2$ were obtained with NbAs by the chemical vapor transport technique. Nb foil (99.9%), grains of high-purity As (99.9999%), and iodine (99.999%) as a transport agent with a molar ratio of 1:1:0.02 were placed in a quartz tube with a diameter of 18 mm, and then the tube was sealed in a vacuum [24]. The staring materials were

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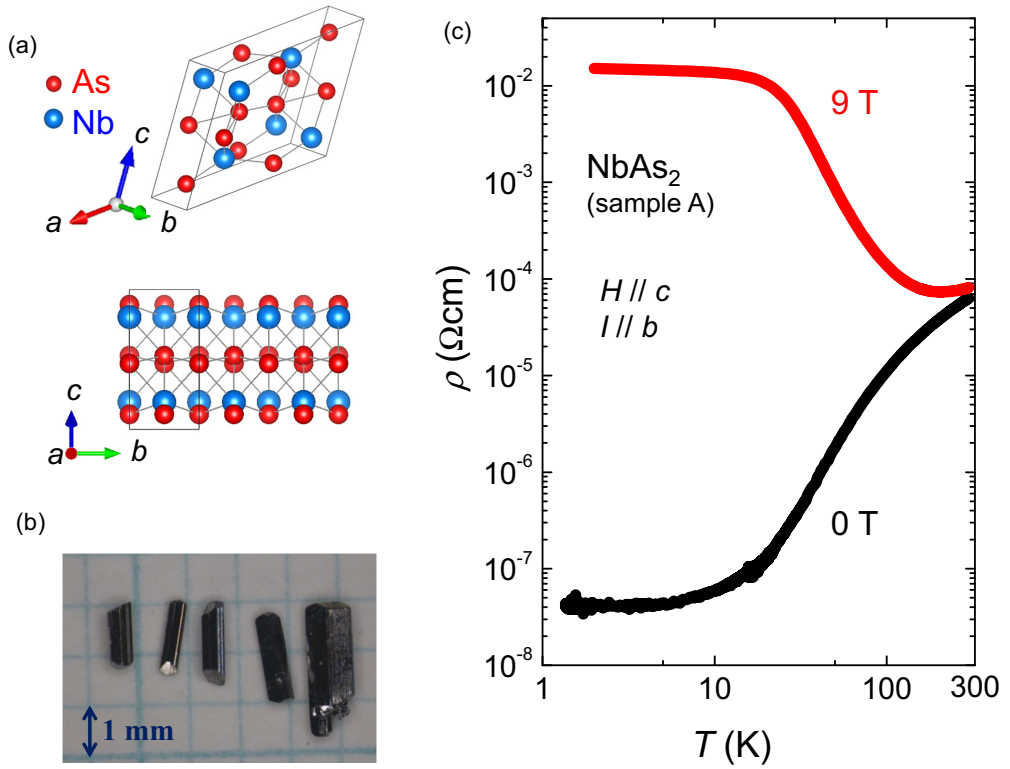

FIG. 1. (a) Crystal structure of $NbAs_2$. (b)Photograph of the single crystals of $NbAs_2$. (c) Temperature dependence of the resistivity of $NbAs_2$ single crystal (sample A) in zero field and in 9 T.

heated at 1050 °C and kept for ten days. Then, the single crystals of $NbAs_2$ with 1 ∼ 2 mm length [Fig. 1(b)] were grown on a side wall in the quartz tube around the reacted NbAs foil, indicating that the $NbAs_2$ crystals were grown from a vapor phase. Chemical vapor growth using Nb foils has the advantage of keeping the inside of the quartz tube clean during the preparation process, and in our case this approach successfully prevented the generation of numerous unnecessary crystal nuclei. In addition, chemical vapor growth without a temperature gradient seems to allow relatively slower crystallization from an incidentally generated crystal nucleus. Electrical resistivity was measured by a four-probe method using silver paste for the electrodes. Depending on the magnitude of the resistivity, excitation current from 1 to 100 mA was applied parallel to the crystalline *b* direction. We confirmed that resistivity measurements were not affected by the Joule heating. A magnetic field was applied along the *c* axis by a superconducting magnet up to 14 T and by a pulse magnet up to 40 T with duration time of 40 msec.

III. RESULTS AND DISCUSSIONS

Figure 1(c) shows the temperature dependence of the electrical resistivity for our best sample (named as A) at 0 T and 9 T. At zero field, the electrical resistivity decreases with decreasing temperature, resulting in a large residual resistivity ratio (RRR) of $\rho(300\ \mathrm{K})/\rho(1.7\ \mathrm{K}) \approx 1{,}580$. The observed residual resistivity of ≈ 41 nΩcm is 7 ∼ 70 times lower than in the previous report for $NbAs_2$ [18–21], indicating that the carrier mobility is significantly enhanced in the present $NbAs_2$. At 9 T, a remarkable increase of resistivity is observed in the low temperature range, which is a typical phenomenon observed in the materials hosting a high carrier mobility. The MR value $\rho(9\ \mathrm{T})/\rho(0\ \mathrm{T}) \approx 3.12 \times 10^5$ at 2 K is about 40 times larger than that previously reported for $NbAs_2$ ($\rho(9\ \mathrm{T})/\rho(0\ \mathrm{T}) \approx 8{,}000$) [19,20].

Figure 2(b) shows a transverse MR of $NbAs_2$ single crystals at 1.7 K in a magnetic field along the crystalline *c* axis, in which the MR takes largest value as shown in Fig. 2(a). The MR shows parabolic dependence on magnetic field and reaches 6.0×10^5 in 14 T at 1.7 K. The MR is hardly dependent on temperature below 4 K. As shown in Fig. 2(c), the MR continues to increase above 14 T and reaches 1.9×10^6 at 40 T. This value is about 15 times larger than the MR for WTe_2 at 0.53 K at 60 T [12]. To the best of our knowledge, such a large MR has never been

TABLE I. Magnetoresistance at 2 K at 9 T, residual resistivity ρ_0, and residual resistivity ratio (RRR) (ρ_{300K}/ρ_{2K}) in several $NbAs_2$ samples. The sample with larger RRR tends to show higher MR and lower ρ_0.

Sample	MR(9 T) at 2 K	ρ_0(Ωcm)	RRR
A	312000	4.1×10^{-8}	1580
B	203000	5.0×10^{-8}	1690
C	116000	3.6×10^{-8}	1360
D	96400	7.8×10^{-8}	1100
E	86900	9.8×10^{-8}	1090
F	79500	1.4×10^{-7}	594
G	52800	1.4×10^{-7}	556
H	36700	1.0×10^{-7}	493

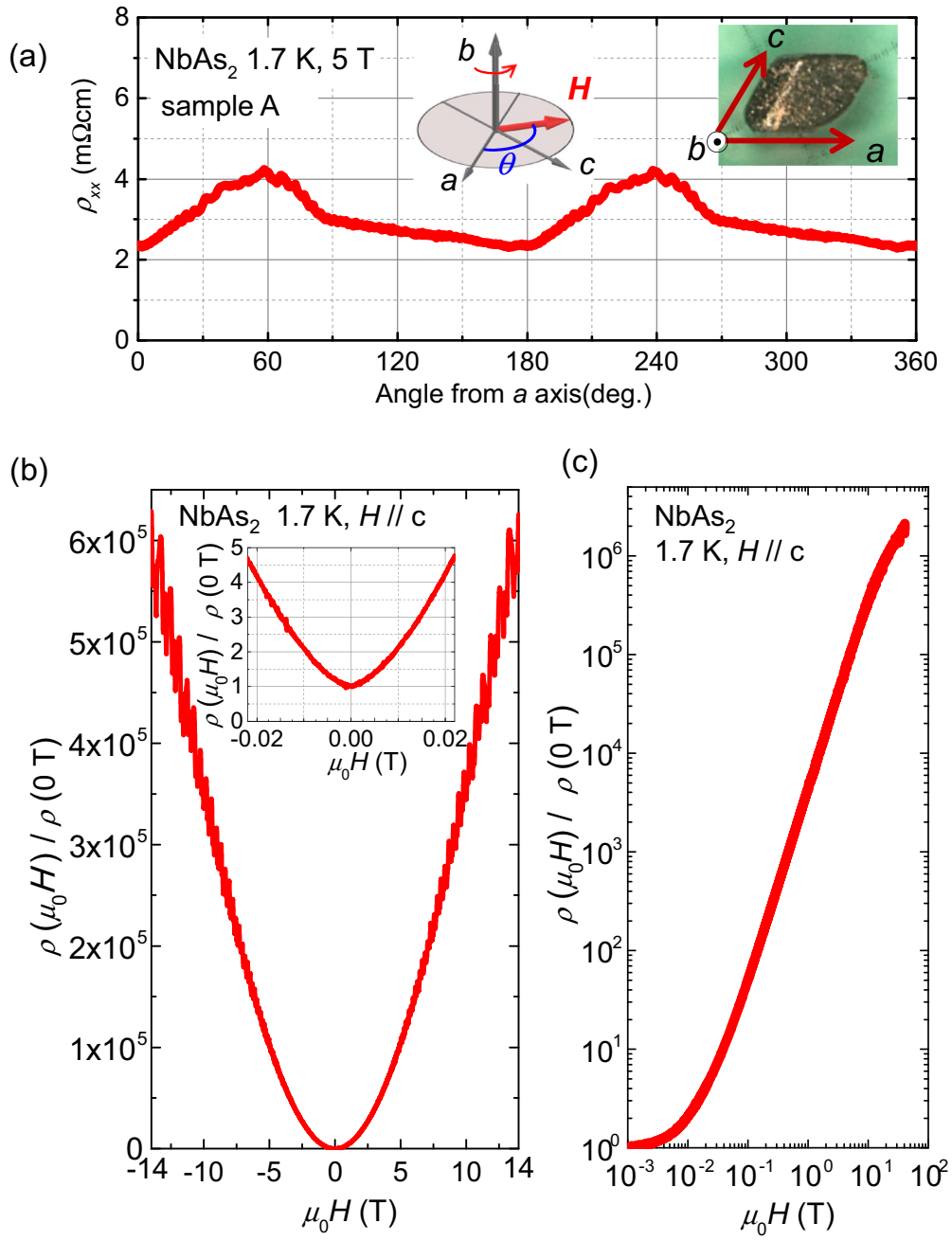

FIG. 2. (a) Angular dependence of ρ_{xx} in $NbAs_2$ (sample A) with rotating magnetic field around b axis. (b) Magnetic-field dependence of $\rho_{xx}(I \parallel b, H \parallel c)$ in a single crystal of $NbAs_2$ (sample A) up to 14 T at 1.7 K. Inset: magnified view of MR in a low-field region. (c) Magnetoresistance up to 40 T at 1.7 K.

reported in a binary semimetal. The MR gradually deviates from the quadratic dependence in a higher field range and still continues to increase above 40 T. Even in a very low field range of 10^{-2} T, MR sensitively increases with increasing magnetic field [inset of Fig. 2(b)]. Here, the residual resistivity was carefully determined by canceling the residual field of 10^{-2} T in a superconducting magnet. We have measured ρ_{xx} in several samples A ∼ H. Those results for MR, residual resistivity, and RRR are shown in Table I.

As shown in Figs. 3(a) and 3(b), the experimental results of ρ_{xx} and ρ_{yx} are well reproduced by the two carrier models [Eqs. (1) and (2)] with $\mu_e = 600{,}000\ \mathrm{cm}^2/\mathrm{Vs}$, $\mu_h = 650{,}000\ \mathrm{cm}^2/\mathrm{Vs}$ (or $\mu_e = 650000\ \mathrm{cm}^2/\mathrm{Vs}$, $\mu_h = 600000\ \mathrm{cm}^2/\mathrm{Vs}$), $n_e = n_h = 1.2 \times 10^{20}\ \mathrm{cm}^{-3}$, and $n_e - n_h = 1.5 \times 10^{17}\ \mathrm{cm}^{-3}$. Here,

$$\rho_{yx} = \frac{1}{e}\frac{\left(\mu_h^2 n_h - \mu_e^2 n_e\right)\mu_0 H + (\mu_e\mu_h)^2(n_h - n_e)(\mu_0 H)^3}{(n_e\mu_e + n_h\mu_h)^2 + (n_e - n_h)^2\mu_e^2\mu_h^2(\mu_0 H)^2}. \quad (2)$$

The carrier densities of $n_e \approx n_h \sim 10^{20}\ \mathrm{cm}^{-3}$ are in agreement with the first principle calculations [20] and are several orders of magnitude higher than those in elemental semimetals. Note that μ_e, μ_h, n_e, and n_h cannot be unambiguously

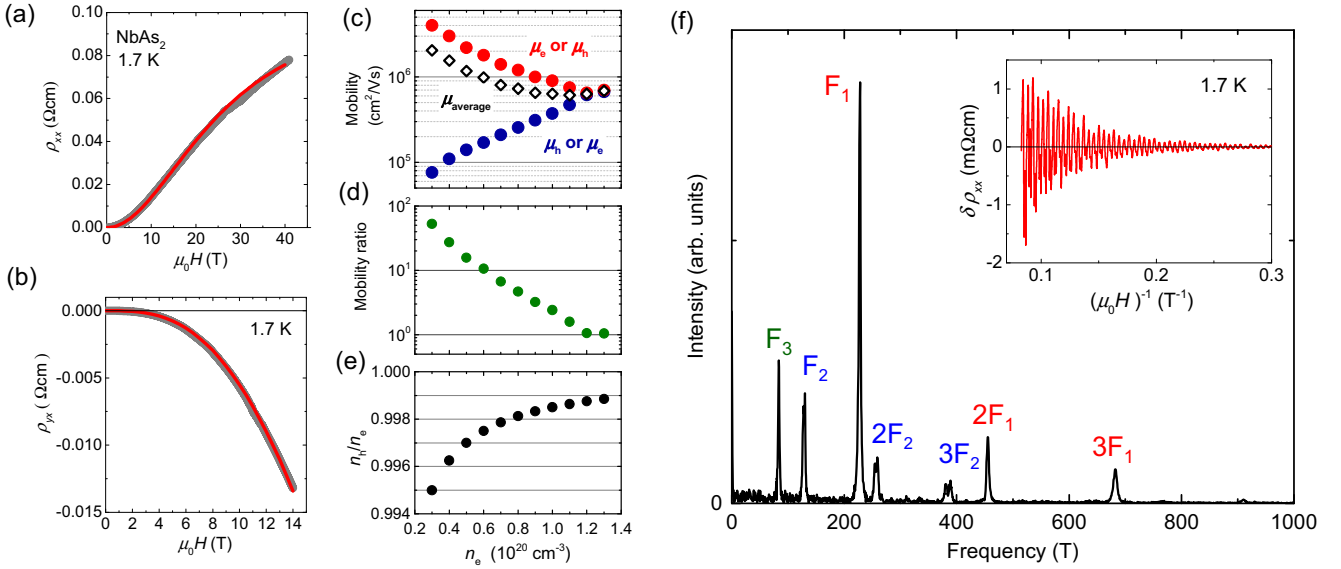

FIG. 3. (a), (b) Two-carrier model fitting of (a) transverse resistivity (ρ_{xx}) up to 40 T and (b) Hall resistivity (ρ_{yx}) up to 14 T at 1.7 K for sample A with $\mu_e = 600{,}000$ cm^2/V·s, $\mu_h = 650{,}000$ cm^2/V·s, $n_h \approx n_e = 1.2 \times 10^{20}$ cm^{-3}, and $n_e - n_h = 1.5 \times 10^{17}$ cm^{-3}. In (a) and (b), the data were smoothed to eliminate the Shubnikov-de Haas (SdH) oscillations. (c)–(e) Carrier-density dependence of (c) μ_h, μ_e, and $\mu_{average}(= (\mu_e + \mu_h)/2)$, which can reproduce the experimental results of ρ_{xx} and ρ_{yx}, (d) mobility ratio, and (e) charge compensation ratio n_h/n_e. Here, $n_e - n_h$ is fixed to be 1.5×10^{17} cm^{-3}. (f) FFT analysis of the SdH oscillations ($\delta\rho_{xx}$) up to 14 T shown in the inset. $\delta\rho_{xx}$ is obtained after subtraction of polynomial background from $\rho_{xx}(\mu_0 H)$.

determined, once large difference between μ_e and μ_h is allowed as shown in Figs. 3(c) and 3(d). Evaluation of the quantum mobility from the Shubnikov-de Haas oscillations [25] seems to be difficult in the large MR system, since the oscillation amplitude is significantly enhanced by the increase of the MR in higher magnetic field, resulting in the apparently higher Dingle temperature and much lower quantum mobility ($\sim 10^3$ cm^2/Vs). Thus, we cannot determine μ_e and μ_h by comparing with the quantum mobility. Taking into account the relatively high FFT frequencies of the Shubnikov-de Haas oscillations in $H \parallel c$ ($F_1 = 227$ T, $F_2 = 128$ T, and $F_3 = 84$ T) shown in Fig. 3(f) as well as those in other directions of H ($F = 40 \sim 700$ T), n_e and n_h in $NbAs_2$ should be higher than 3×10^{19} cm^{-3}. On the other hand, n_e and n_h should be lower than 1.3×10^{20} cm^{-3} to reproduce the residual resistivity with use of the mobilitiy values obtained from the fitting. While the difference between the hole and electron densities ($n_e - n_h \sim 10^{17}$ cm^{-3}) is on the order of that in elemental semimetals, the charge compensation ratio of $n_h/n_e = 0.994 \sim 0.999$ is much closer to 1 than those in elemental semimetals owing to the higher carrier density. Thus, both the high carrier mobilities and high charge compensation are responsible for the present significant enhancement of MR in $NbAs_2$. Application of a pressure to change the size of the Fermi surfaces may be a potential approach for further enhancement of the MR.

In Fig. 4, we plot the MR values $\rho(\mu_0 H)/\rho(0\,\mathrm{T})$ below 4.2 K for various semimetals as a function of magnetic field. Typical values of MR in the recently reported binary semimetals (closed circles) range from 10^3 to $< 10^4$ at 10 T below 4.2 K. These binary systems show much smaller MR than those in elemental semimetals (open circles), owing to the relatively lower carrier mobility. On the other hand, the MR of the present $NbAs_2$ is one or two orders of magnitude larger than that for the binary systems in all the field ranges up to 40 T. Moreover, the MR in the present $NbAs_2$ is comparable to those in elemental systems. Thus, the present results demonstrate the significant enhancement of MR for a binary semimetal by the

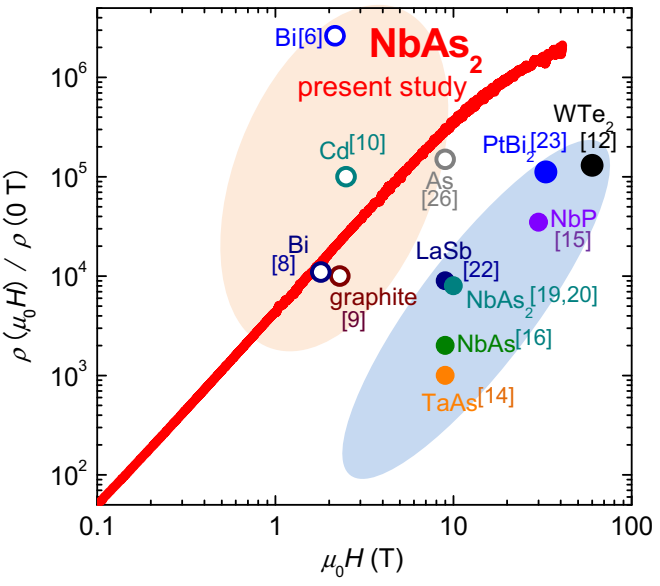

FIG. 4. Magnetoresistance in $NbAs_2$ (sample A) and representative semimetals exhibiting large MR. Typical area of MR in elemental (open circles) and binary semimetal (closed circles) in the previous reports are shown by different colors.

improvement of the crystal quality, which may open up a new class of large MR materials.

IV. CONCLUSIONS

In summary, we have found an extremely large MR exceeding 1.9 million in a single crystal of $NbAs_2$ at 40 T at 1.7 K. The magnitude of MR is several tens of times larger than those in recently reported binary semimetals and comparable to those of ultrahigh mobility elemental semimetals. Moreover, the MR shows no saturation up to 40 T. The almost full charge compensation and ultrahigh mobility in the present $NbAs_2$ crystal are the origin of the dramatic enhancement of the MR. A binary semimetal with higher carrier densities has a great advantage for achieving a full charge compensation, and therefore has great potential for further enhancing the MR through an improvement of crystal quality.

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