Antiferromagnetic transitions in the Kondo lattice system $Ce_2Ni_3Ge_5$

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Our investigation of $Ce_2Ni_3Ge_5$ by means of transport, specific heat and magnetization measurements shows that the compound is a Kondo lattice system exhibiting two antiferromagnetic transitions at $T_{N1}=5.1$ K and $T_{N2}=4.5$ K. An analysis of the transport and specific heat data suggests that the Kondo energy scale k_BT_K is of the order of k_BT_N. The resistivity and heat capacity data below 4 K are suggestive of the appearance of a spin-wave gap. The compound exhibits giant magnetoresistance at low temperature. The crystal field splitting is estimated to be about 180 K.

I. INTRODUCTION

Ce-based intermetallic compounds exhibit a wide range of magnetic behavior such as magnetic ordering, the Kondo effect, heavy-fermion behavior, and valence fluctuation, which arise from the competition between RKKY and Kondo interactions. $CeAl_2$ and CeB_6 are typical examples of a Kondo-type antiferromagnetic; $CeCu_6$ is a heavy-fermion system with a nonmagnetic ground state, and $CeCu_2Si_2$ is a heavy-fermion superconductor.[1–4] $Ce_2Ni_3Ge_5$ is a member of the $R_2M_3X_5$ ($R=$rare earth, $M=$transition metals, $X=$Si, Ge) series of compounds which have shown many interesting properties. For example, $R_2Fe_3Si_5$($R=$Sc, Y, Lu) show superconductivity even in the presence of a large fraction of Fe in the materials.[5] $Tm_2Fe_3Si_5$ is an antiferromagnetic superconductor[6] showing reentrance to the normal state below T_N; $U_2Rh_3Si_5$ undergoes a simultaneous spin-quadrupolar ordering.[7] The investigation of $Ce_2Ni_3Ge_5$ is important also from the point of view that the structurally related compound $CeNi_2Ge_2$ shows non-Fermi-liquid behavior and the signature of superconductivity.[8]

In this paper we report the magnetic and transport properties of $Ce_2Ni_3Ge_5$. The existence of $Ce_2Ni_3Ge_5$ with $U_2Co_3Si_5$-type crystal structure was reported by Morozkin and Seropegin.[9] Isostructual $Ce_2Ni_3Si_5$ is known to be a valence fluctuating compound.[10] Since the replacement of Si by Ge will reduce the hybridization, $Ce_2Ni_3Ge_5$ is expected to show heavy-fermion behavior or to be a Kondo lattice which undergoes magnetic ordering. Such speculation was experimentally found to be true in CeM_2X_2 ($M=$transition metal, $X=$Si, Ge) compounds.[11,12] Indeed, recently, Chavelier *et al.*[13] observed magnetic ordering at 4.2 K in $Ce_2Ni_3Ge_5$ using a magnetic susceptibility measurement.

II. EXPERIMENT

Polycrystalline samples were prepared using the standard arc melting technique. The samples were annealed at 900 °C for 1 week. Electrical resistivity measurements were carried out using the conventional dc four-probe technique. The heat capacity was measured using an adiabatic heat pulse method. A commercial superconducting quantum interference device (SQUID) magnetometer was used for the magnetization measurement. Magnetoresistance measurements were carried out using a physical property measurement system (Quantum Design). All measurements have been carried out on two independently prepared samples which show similar behavior.

III. RESULTS AND DISCUSSION

The powder x-ray diffraction, metallographic examination, and the electron probe microanalysis (EPMA) results show that the sample is single phase and it crystallizes in $U_2Co_3Si_5$-type orthorhombic structure (spacegroup *Ibam*) with lattice parameters $a=9.814$ Å, $b=11.844$ Å, and $c=5.963$ Å. The unit cell volume of $Ce_2Ni_3Ge_5$ is 693.12 Å^3, which is 9.6% larger than that of $Ce_2Ni_3Si_5$. The Ce atoms occupy only one type of site in this structure.

As shown in Fig. 1, at high temperatures ($T>50$ K), the susceptibility follows Curie-Weiss behavior with $\mu_{eff}=2.5\,\mu_B$, which is close to the value expected for Ce^{3+} ions. The paramagnetic Curie temperature (θ_p) was found to be -52 K. Such a large negative value of the Curie temperature is often found in Kondo compounds. Two anomalies at 4.5 and 5.1 K are observed, indicating antiferromagnetic ordering. The isothermal magnetization (at 4.4 K) is linear and reversible up to 5.5 T, which is consistent with the antiferromagnetic nature of the magnetic ordering. The increase of susceptibility between 4.5 and 5.1 K is possibly due to the incommensurate nature of the antiferromagnetic ordering at 5.1 K. We wish to mention here that Chevalier and Etourneau found only one magnetic transition[13] at 4.2 K in $Ce_2Ni_3Ge_5$. We have been able to detect two magnetic transitions using a smaller temperature interval for the data points. Since our sample is of high quality as revealed by metallographic examination, EPMA, and the large value of the residual resistivity ratio (RRR~40), we believe both magnetic transitions are intrinsic.

The resistivity shows a weak temperature dependence

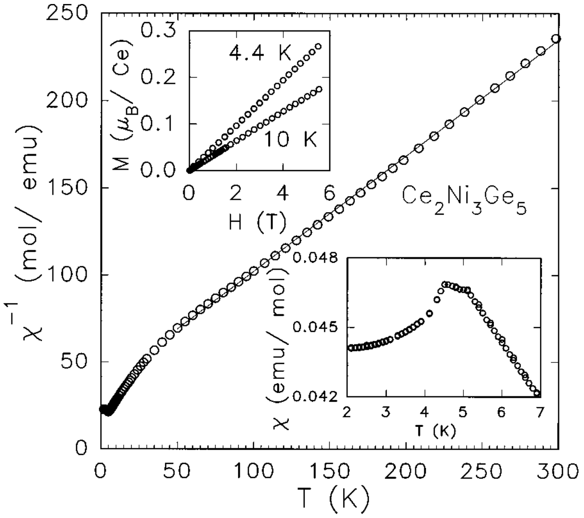

FIG. 1. Inverse susceptibility (χ^{-1}) as a function of temperature for $Ce_2Ni_3Ge_5$ measured in a field of 0.1 T. The insets show χ vs T at low temperatures and isothermal magnetization at 4.4 and 10 K.

down to 100 K and a minimum at ~30 K (Fig. 2). It shows a change of slope at 5.1 K and a strong decrease below 4.5 K which are associated with the two magnetic phase transitions as revealed by the magnetic susceptibility measurement. The resistivity ratio between 5.1 and 1.5 K is $\rho_{mag}(5.1\,K)/\rho_{mag}(1.5\,K)=66$, and the total drop of resistivity is more than 175 $\mu\Omega$ cm. Large values of the drop of resistivity have recently been observed in $Ce_2Rh_3Ge_5$ and $Ce_2Ir_3Ge_5$ and also in $U_2Rh_3Si_5$.[14,7] For the former two compounds, the large drop was attributed to the combined effect of the reduction of spin-disorder scattering and the development of coherence. In $U_2Rh_3Si_5$ a simultaneous spin-quadrupolar ordering takes place below 25 K and the resistivity data suggest the appearance of a spin-wave gap. As in the case of $U_2Rh_3Si_5$, resistivity data of $Ce_2Ni_3Ge_5$ below 4 K can be fitted as $\rho(T)=\rho_0+AT^2+CT(1+2T/E_g)\exp(-E_g/T)$, where ρ_0 is the residual resistivity, AT^2 is the Fermi liquid contribution, and E_g is the gap in the spin-wave spectrum. The spin-wave gap is estimated to be 12 K.

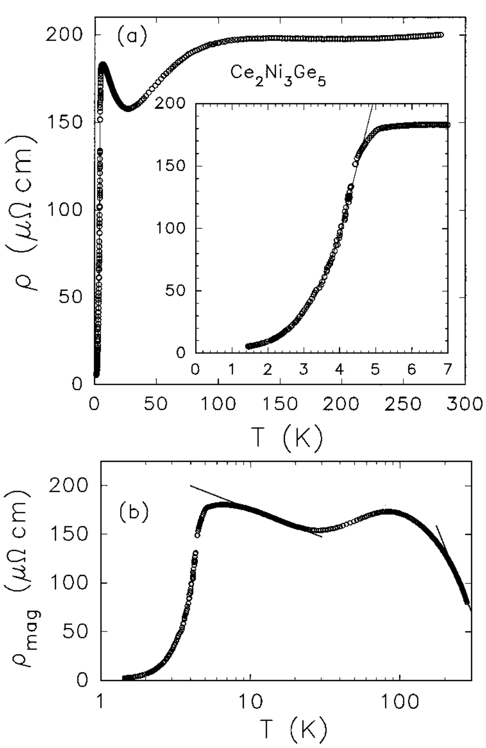

FIG. 2. (a) Electrical resistivity of $Ce_2Ni_3Ge_5$ in the temperature interval 1.3–300 K. The inset shows an expanded view of the low-temperature part of the resistivity. The solid line is the fit to the data below 4 K (see text). (b) Magnetic contribution to the electrical resistivity ρ_{mag} vs $\ln T$.

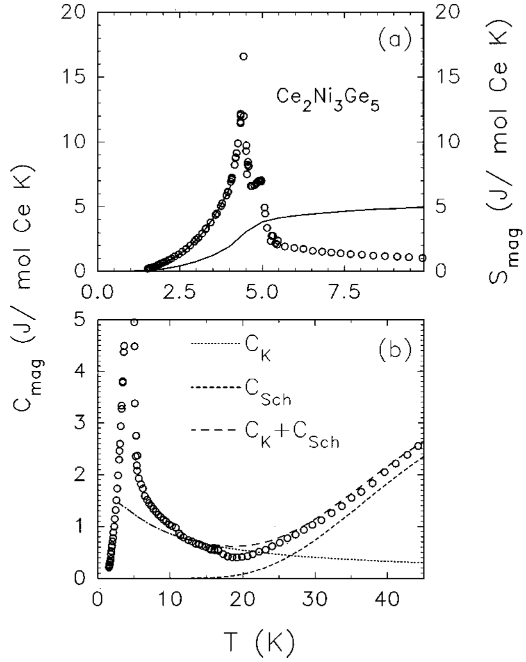

FIG. 3. (a) Heat capacity and magnetic entropy of $Ce_2Ni_3Ge_5$ as a function of temperature. Large anomalies due to magnetic transitions are seen at low temperature. The solid line passing through the data points represents a fit to the expression mentioned in the text. (b) Magnetic contribution to the heat capacity together with the calculated values of the Kondo and Schottky contributions to the heat capacity.

The magnetic part of the resistivity, ρ_{mag}, which is obtained by subtracting the resistivity data of $La_2Ni_3Ge_5$, behaves as (-ln T) in two different temperature regions [Fig. 2(b)]. Such behavior is expected for Kondo-type interactions in the presence of crystal field effects.[15] The high-temperature logarithmic regions represent the Kondo effect in the excited doublet, whereas the low-temperature regions represent the Kondo effect from the crystal field ground state. These regions are separated by a maximum whose temperature is related to the crystal field splitting. Thus the resistivity data suggest a crystal field spitting of ~100–200 K for the excited doublet in this compound.

In Fig. 3 we have plotted the magnetic part of the heat capacity which is obtained by subtracting the heat capacity of $La_2Ni_3Ge_5$ from that of $Ce_2Ni_3Ge_5$. Two peaks are observed at ~4.5 and ~5 K which are due to the magnetic ordering. The total jump in the heat capacity is more than 15 J/Ce mol K, which is larger than what is expected on the basis of mean field theory. Further, the peak in the low temperature (~4.5 K) is quite sharp (full width at half maximum, FWHM = 0.1 K). These two facts hints at the first-order nature of the magnetic phase transition at 4.5 K. We wish to point out here that we could not detect any hysterisis in the resistivity measurement at low temperature within our temperature resolution of 50 mK. This, however, does not rule out the possibility of the first-order nature of the magnetic transition at 4.5 K. In the case of $U_2Rh_3Si_5$ no hysterisis could be detected in the resistivity measurement, but the first-order nature of the magnetic transition was established from neutron diffraction and thermal expansion measurements.[7] Similar measurements are desired to establish the first-order nature of the magnetic phase transition at 4.5 K in $Ce_2Ni_3Ge_5$. The magnetic entropy at T_N (5.1 K) reaches $0.67R \ln 2$. Thus there is a considerable reduction of the magnetic entropy due to the Kondo effect. In the absence of short-range order, a plausible reason for the deficiency of the $S_{\mathrm{mag}}(T_N)$ is that the twofold degeneracy is partially lifted above T_N by the presence of the Kondo effect. In such a case it can be shown that $S_{\mathrm{mag}}(T_N)=S_K(T_N/T_K)$, where $S_K(T_N/T_K)$ is the Kondo entropy at T_N.[16] Two conditions are necessary for this relation to hold good: (i) $\Delta_{\mathrm{CF}} \gg k_B T_N$ and (ii) $\Delta_{\mathrm{CF}} \gg k_B T_K$. From the resistivity and magnetic susceptibility data, we have seen that both conditions are satisfied for $Ce_2Ni_3Ge_5$. Further, using the Bethe ansatz for a spin-$\frac{1}{2}$ Kondo model, Desgranges and Schotte calculated the specific heat and magnetic entropy.[17] The above relation provides the ratio T_N/T_K using the experimentally found $S_{\mathrm{mag}}(T_N)$.[17] Using this method, we estimate the Kondo temperature to be $\sim$5 K. We attribute the entropy reduction to be due to the Kondo effect only. This assumption is reasonable since we do not see any tail in the heat capacity above the magnetic ordering temperature. In the temperature range 1.5–4.0 K, the magnetic part of the heat capacity could be fitted as $C_{\mathrm{mag}}(T)=\gamma T+\beta T^3 \exp(-E_g/k_B T)$, which corresponds to the antiferromagnetic magnon spectrum with an energy gap as also indicated by the resistivity data. The spin-wave gap, however, is found to be much less ($\sim$2 K) from the heat capacity data as compared to 12 K from the resistivity data. The γ value is found to be rather large, $\sim 90\,\mathrm{mJ/mol\,Ce\,K^2}$, but C_p data at lower temperature would be necessary to perform a more precise determination. The magnetic contribution to the heat capacity in the paramagnetic region is well accounted for by a combination of Kondo-type and Schottky-type contributions [Fig. 3(b)]. The Kondo contribution to the heat capacity was taken from Ref. 17. $T_K=5$ K, estimated from the magnetic entropy, was used to calculate the Kondo contribution. The simulation of the heat capacity data leads to a crystal field splitting of $\sim$180 K.

Two magnetic phase transitions have also been seen in the antiferromagnetic Kondo lattice CePtSn.[18] The magnetic structure is incommensurate to the lattice in both antiferromagnetic phases.[19] It remains to be seen whether the antiferromagnetic structure remains incommensurate in both phases in $Ce_2Ni_3Ge_5$ also or undergoes a transition from an incommensurate to a commensurate structure at lower temperatures as observed in $Tb_2Fe_3Si_5$.[20] As crystallographically all the Ce ions are equivalent, the two magnetic phase transitions are associated with a change of the magnetic structure.

Since the magnetic field can also influence the arrangement of the magnetic spins, it is interesting to see the effect of the magnetic field on the magnetic transitions in $Ce_2Ni_3Ge_5$. We notice that with an increase of field both T_{N1} and T_{N2} decrease [Fig. 4(a)], which is consistent with the fact that phase transitions at T_{N1} and T_{N2} are both of antiferromagnetic nature. The field dependence of T_{N1} and T_{N2} is shown in Fig. 5. The resistivity data as a function of field at constant temperatures are shown in Fig. 4(b). The most interesting aspect of the field dependence of the resistivity is a sharp rise at a critical field value $B_c(T)$ which decreases with increasing temperature and disappears at T_{N2} (4.5 K). $B_c(T)$ is also plotted together with T_{N1} and T_{N2} in Fig. 5. It is clear from this figure that the sharp rise of resistivity is associated with the second magnetic transition (at T_{N2}). Such a drastic increase of resistivity at a particular field is rarely observed. It is not associated with a metamagnetic transition

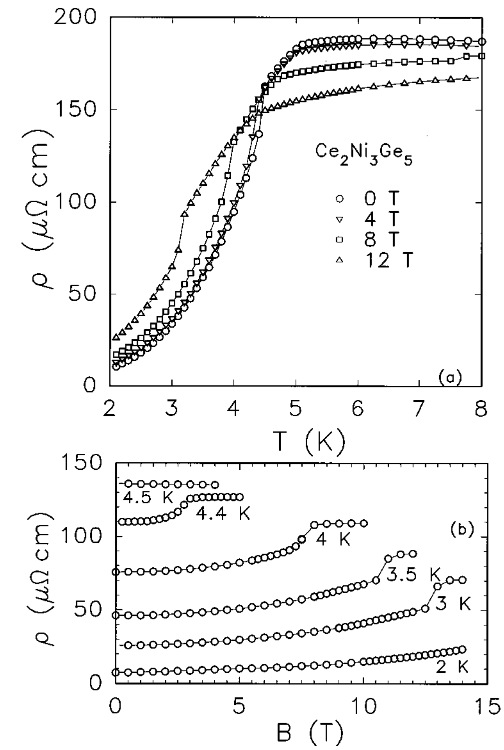

FIG. 4. Resistivity (a) as a function of temperature at various fixed field and (b) as a function of field at various fixed temperature.

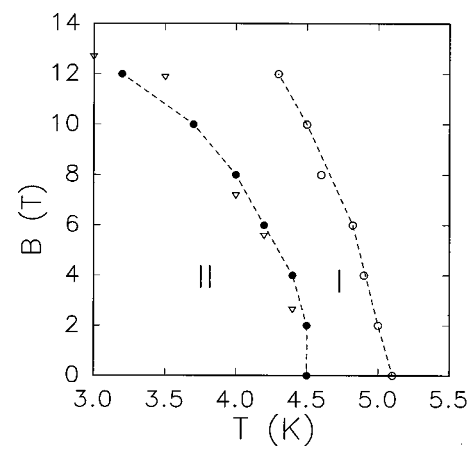

FIG. 5. *B-T* phase diagram of $Ce_2Ni_3Ge_5$. T_{N1} and T_{N2} are represented by open and solid circles. Dashed lines are a guide for the eye. The critical fields at which a sharp increase in resistivity is seen [see Fig. 4(b)] are denoted by open triangles.

since at 4.4 K we see a large increase of the resistivity at ~2.5 T, whereas the magnetization is strictly linear up to 5.5 T. Further, usually a metamagnetic transition results in a drop of resistivity, leading to negative magnetoresistance. The resistivity of $Ce_2Ni_3Ge_5$ as a function of field and temperature hints at a rearrangement of the Fermi surface at T_{N2}. It is also clear from Fig. 4(a) that the magnetoresistance is positive in the magnetically ordered state, whereas it is negative in the paramagnetic state. The positive magnetoresistance in the ordered state is consistent with the antiferromagnetic nature of the magnetic ordering. The destruction of the coherent state by the application of magnetic field could also add up, leading to a giant positive magnetoresistance (220% at 2 K and 14 T).

In the paramagnetic region the negative magnetoresistance is due to the freezing out of spin-flip scattering in a Kondo compound by the magnetic field. The normalized magnetoresistance in the paramagnetic region could be mapped onto a single curve by scaling the field values at different temperatures as $B/(T+T^*)$ where T^* is the characteristic temperature which is an approximate measure of the Kondo temperature[21] (see Fig. 6). We estimate the Kondo temperature from such scaling to be ~6 K. This value is in agreement with T_K~5 K estimated from the reduction of magnetic entropy due to the Kondo effect.

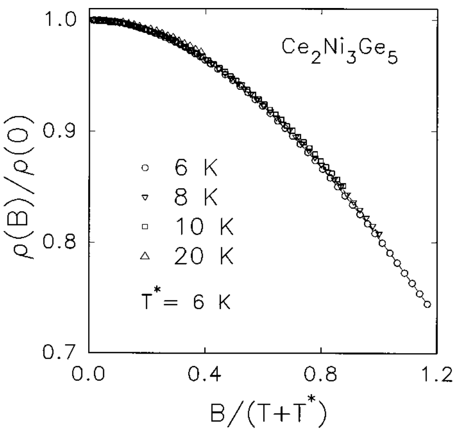

FIG. 6. Normalized resistivity plotted as a function of $B/(T+T^*)$, where T^* is the characteristic temperature.

IV. CONCLUSION

The resistivity, magnetic susceptibility, heat capacity and magnetoresistance data without any ambiguity establish that $Ce_2Ni_3Ge_5$ is a Kondo lattice compound which undergoes successive magnetic phase transitions at 4.5 and 5.1 K. The magnetic entropy at T_N is only $0.67R \ln 2$, which is suggestive of the reduction of the magnetic moment due to the Kondo effect. The peak in the susceptibility with no difference between the zero-field-cooled and field-cooled values and the linear behavior of the magnetization are suggestive of the antiferromagnetic nature of the magnetic ordering. Positive magnetoresistance at 2 K is also consistent with the antiferromagnetic nature of the magnetic phase transition. The resistivity and heat capacity data below 4 K indicate the appearance of a spin-wave gap. The crystal field splitting is estimated to be ~180 K. The Kondo temperature in the crystal-field-split ground state is ~5 K. Further investigations are necessary to determine the nature of the low-temperature magnetic structure and the crystal field level scheme.

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[1] B. Barbara, J. X. Boucherle, J. L. Buevoz, M. F. Rossignol, and J. Schweizer, Solid State Commun. **24**, 481 (1977).
[2] T. Komatsubara, T. Suzuki, M. Kawakami, S. Kunii, T. Fujita, Y. Ishikawa, A. Takase, K. Kojima, M. Suzuki, and T. Kasuya, J. Magn. Magn. Mater. **15–18**, 963 (1980).
[3] Y. Onuki, Y. Shimizu, and T. Komatsubara, J. Phys. Soc. Jpn. **53**, 1210 (1984).
[4] F. Steglich, J. Aarts, C. D. Bredl, W. Licke, D. Meschede, W. Franz, and J. Schafer, Phys. Rev. Lett. **43**, 1892 (1979).
[5] H. F. Braun, Phys. Lett. **75A**, 386 (1980).
[6] C. U. Segre and H. F. Braun, Phys. Lett. **85A**, 372 (1981).
[7] B. Becker, S. Ramakrishnan, A. A. Menovsky, G. J. Nieuwenhuys, and J. A. Mydosh, Phys. Rev. Lett. **78**, 1347 (1997).
[8] P. Gegenwart, F. Kromer, M. Lang, G. Sparn, C. Geibel, and F. Steglich, Phys. Rev. Lett. **82**, 1293 (1999).
[9] A. V. Morozkin and Yu. D. Seropegin, J. Alloys Compd. **237**, 124 (1996).
[10] C. Mazumdar, R. Nagarajan, S. K. Dhar, L. C. Gupta, R. Vijayaraghavan, and B. D. Padalia, Phys. Rev. B **46**, 9009 (1992).
[11] C. Amarguellat, M. Escorne, A. Maugar, E. Beaurepaire, M. F. Ravel, G. Krill, F. Lapiere, P. Haen, and C. Godart, Phys. Status Solidi B **143**, 159 (1987).
[12] G. Knopp, A. Loidl, R. Caspary, U. Gottwick, C. D. Bredl, H. Spille, F. Steglich, and A. P. Murani, J. Magn. Magn. Mater. **74**, 341 (1998).
[13] B. Chevalier and J. Etourneau, J. Magn. Magn. Mater. **196–197**, 880 (1999).
[14] Z. Hossain, H. Ohmoto, K. Umeo, F. Iga, T. Suzuki, T. Takabatake, N. Takamoto, and K. Kindo, Phys. Rev. B **60**, 10 383 (1999).
[15] B. Cornut and B. Coqblin, Phys. Rev. B **5**, 4541 (1972).
[16] H. Mori, H. Yashima, and N. Sato, J. Low Temp. Phys. **58**, 513 (1985).
[17] H.-U. Desgranges and K. D. Schotte, Phys. Lett. **91A**, 240 (1982).
[18] T. Takabatake, H. Iwasaki, G. Nakamoto, H. Fuji, H. Nakotte, F. R. de Boer, and V. Sechovsky, Physica B **183**, 108 (1993).
[19] H. Kadowaki, T. Ekino, H. Iwasaki, T. Takabatake, H. Fuji, and J. Sakurai, J. Phys. Soc. Jpn. **62**, 4426 (1993).
[20] A. R. Moodenbaugh, D. E. Cox, and H. F. Braun, Phys. Rev. B **25**, 4702 (1982).
[21] P. Schlottmann, Z. Phys. B: Condens. Matter **51**, 223 (1983).