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Temperature Dependence of the First- and Second-Order Cubic Anisotropy Constants in EuSe[†]

Glen E. Everett and Ray C. Jones*
Physics Department, University of California, Riverside, California 92502

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The first- and second-order cubic anisotropy constants in EuSe have been measured as a function of temperature from 1.15 to 10 °K. Ferromagnetic resonance measurements at K-band frequencies (24 GHz) assured single-domain samples and internal fields high enough to produce the ferromagnetic phase over the entire temperature range. The results show structure in addition to a very weak temperature dependence below the zero-field ordering temperature (4.6 °K). The results are not explained by a single-ion theory of anisotropy. Changes in the anisotropy constants as well as the linewidth correspond in temperature to observed zero-field phase changes, indicating that the current description of EuSe, as being in a simple ferromagnetic phase for $\vec{H}_{int} > 2$ kOe, is incomplete.

I. INTRODUCTION

The divalent europium chalcogenides are fcc insulating compounds which order magnetically at low temperatures. The ground state of the Eu^{2+} ion is $^8S_{7/2}$. From measurements of the high-temperature paramagnetic resonance linewidth and the result $g = 2.0$, it was first shown by von Molnar and Lawson[1] for EuS that the classical coupling constant described adequately the magnetic dipolar interaction in this material and that pseudodipolar effects were not important. This has been shown experimentally to be true, subsequently, in all of these compounds.[2] The dipolar contribution to the first-order cubic anisotropy constant K_1 can be calculated at 0 °K for a ferromagnetic system using Van-Vleck's theory[3] and shown to be much smaller than the experimentally determined values in EuO,[4] EuS,[5] and EuSe.[6] (EuTe is antiferromagnetic and must be considered separately.) The magnetic anisotropy energy in these compounds has been attributed to the interaction of each ion with the local crystalline electric field, the Wolf single-ion mechanism[7] as extended by von Molnar[8] to include the higher-order terms in the spin Hamiltonian appropriate to the Eu^{2+} ion. The values of the crystal-field parameters b_4 and b_6 obtained by interpreting the measured low-temperature values of the first- and second-order cubic anisotropy constants, K_1 and K_2, in terms of a single-ion theory, were consistent with but smaller than the results obtained for dilute concentrations of Eu^{2+} ions in various cubic host lattices.

A more critical test of the single-ion mechanism being the source of the magnetic anisotropy energy is provided by measuring its thermal variation. Miyata and Argyle[4] measured $K_1(T)$ in EuO and concluded that the single-ion theory described very well their results. Subsequently, Hughes[9] has measured, using a ferromagnetic resonance technique, the variation of both K_1 and K_2. The results for K_1 were in essential agreement with the conclusions of Miyata and Argle[4] but the results for $K_2(T)$ deviated from the predictions of a single-ion theory. Everett and Ketcham[10] have measured the variation of K_1 and K_2 in EuS finding that neither K_1 nor K_2 is well described by the single-ion model alone. They suggest that their results indicate that the anisotropy energy is the result of at least two contributing mechanisms, for which linear magnetostriction is the most likely second contribution. They were not able to make a quantitative estimate since the magnetoelastic constants of EuS have not been determined.

The previous measurement of K_1 and K_2 in EuSe[6] was at a single temperature, the values of b_4 and b_6 being thus uniquely determined. It was therefore desirable to measure these quantities versus temperature to determine whether or not a simple single-ion description is adequate for this material. The results of our measurements (Sec. III) indicate that the single-ion mechanism is totally inadequate. Since EuSe is known to have many unusual properties, we will review briefly what is known about this material.

EuSe is characterized by two ordering temperatures in zero magnetic field—2.8 and 4.6 °K.[11] With decreasing temperature the transition at 4.6 °K is from the paramagnetic to the antiferromagnetic (AFM) state while the transition at 2.8 °K is from an AFM to a two-component phase consisting of ferrimagnetic and AFM contributions. The transition at 2.8 °K is observed as a small cusp in the specific heat[11] and as a change in sign of the temperature derivative of the initial susceptibility $(\partial\chi/\partial T)_{\vec{H}\to 0}$.[12] Measurements of the magnetization $\vec{M}$ versus field show that $\vec{M}$ increases rapidly until a field $\vec{H}_1$ is reached. Above $\vec{H}_1$ and below a second field $\vec{H}_2$ the change in $\vec{M}$ is small suggesting a state of intermediate saturation. Above $\vec{H}_2$, $\vec{M}$ again increases rapidly and approaches ferromagnetic saturation in applied fields of 7–8 kOe. With minor differences, the same behavior is observed on single crystals for the field applied along a ⟨100⟩, ⟨110⟩, or ⟨111⟩ direction.[13] Neutron-diffraction experiments[14] on single-crystal samples in zero magnetic field have identified the phase existing between 2.8 and 4.6 °K as being AFM. Below 2.8 °K, new lines were observed in addition to those of the AFM phase. The additional phase, coexisting with the AFM, has a ferrimagnetic character and a spin structure has been proposed.

Kuznia and Kneer[15] interpreted the fields $\vec{H}_1$ and $\vec{H}_2$ bounding the state of intermediate magnetic saturation as being the fields which induce a transition from the AFM to ferrimagnetic and from the ferrimagnetic to a ferromagnetic phase, respectively. They measured the temperature dependence of these fields and proposed a $(\vec{H}, T)$ magnetic phase diagram. Schwob[16] has examined the various experimental data and combined them with his results and gives a more recent version of this phase diagram. At high fields (10 kOe) measurement of the magnetization versus temperature has shown $\vec{M}$ to follow a Brillouin-function dependence.[17] From Schwob's[16] diagram we would thus expect that for internal fields greater than ~2 kOe EuSe should be ferromagnetic at all temperatures below the ordering temperature $T_0 \simeq 4.6$ °K. For our resonance determination of the anisotropy constants, the internal field $\vec{H}_i = \vec{H}_a - \frac{4}{3}\pi\vec{M}_0$ is about 4 kOe and thus twice the value required to insure the samples being in a pure ferromagnetic phase. We would thus expect that the formalism of the Wolf[7] single-ion model for anisotropy would describe EuSe.

II. EXPERIMENTAL TECHNIQUES

Polycrystalline EuSe was synthesized by the direct reaction of the elements in an evacuated sealed quartz tube. The compound was subsequently subjected to a fractional distillation in a high-purity graphite crucible. The material was sublimed at a temperature of ~1525 °C. In condensing, single-crystal grains were formed which though small (cubes ~0.4 mm on an edge), could be ground into spheres and used for the resonance measurements. After grinding and polishing, they were annealed to relieve any induced strain, x-ray oriented, and transferred to the sample holder for measurement.[6]

The anisotropy constants K_1 and K_2 were determined from measurements of the angular dependence of the ferromagnetic resonance field at constant frequency. For a cubic system, the anisotropy energy can be represented by

$$E_A = K_1(\gamma_1^2\gamma_2^2 + \gamma_2^2\gamma_3^2 + \gamma_3^2\gamma_1^2) + K_2\gamma_1^2\gamma_2^2\gamma_3^2, \quad (1)$$

where the terms γ_i are the direction cosines of the magnetization vector $\vec{M}$ with respect to the three cube edges of the unit cell. For $\vec{H}$ lying in a {110} plane, the angular dependence of the resonant field to first order in the ratios $\Delta_1 = K_1/MH_0$ and $\Delta_2 = K_2/MH_0$ can be written as

$$H(\varphi) = \sum_{n=0}^{3} H_{2n} \cos 2n\varphi, \quad (2)$$

where φ is the angle between the applied field and a ⟨100⟩ direction,[18] and Δ_1, $\Delta_2 \ll 1$. The constants H_4 and H_6 of Eq. (2) depend on a linear combination of K_1 and K_2 and just K_2, respectively. An harmonic analysis of the data permits a determination of K_1 and K_2. (The actual quantities determined directly are the ratios K_1/M and K_2/M.) The microwave spectrometer and cryogenic system used were of standard design.[9] The klystron was frequency stablized to the resonant cavity assuring measurements of just the absorptive mode. All measurements were made in a resonant cavity operating at 24.0 GHz. The cavity was surrounded by a double can arrangement which was immersed directly in liquid helium. The inner can was filled with helium gas at a pressure of ~0.1 torr for thermal contact with the sample while the outer can was evacuated. Temperature was controlled electronically with an integrating-plus-proportional controller using a carbon resistor as the sensing element. The long-term drift and short-term fluctuations in temperature were less than 0.01 °K. Temperature was measured with an independent-calibrated carbon resistor to an estimated accuracy of ± 0.01 °K. At each temperature the ferromagnetic resonance absorption line was measured as a function of incident microwave power. In this way power levels sufficiently low to avoid linewidth broadening and sample-heating effects were determined and used for all of the anisotropy constant determinations.

The high signal-to-noise ratio of our system permitted the use of the measured derivative of the absorbed power with respect to field, $dP/d\vec{H}$, in a feedback loop through the magnet controller. In this way, the magnetic field was set to the value required for resonance automatically, greatly faccilitating the speed and precision of data acquisition. At each temperature, the resonant field was measured at 90 angles spaced equally in the interval 0°–180°. (The crystallographic directions were determined directly from the symmetry of the measured angular dependence.) The uncertainty in the individual field measurements was ± 0.1 Oe at the lowest temperatures and increased with increasing linewidth to ±1.0 Oe at 10 °K. We have estimated the absolute uncertainties as being $\Delta K_1/M = \pm 0.5$ G and $\Delta K_2/M = \pm 2$ G, while the relative uncertainty of these quantities as a function of temperature is lower. A more complete discussion

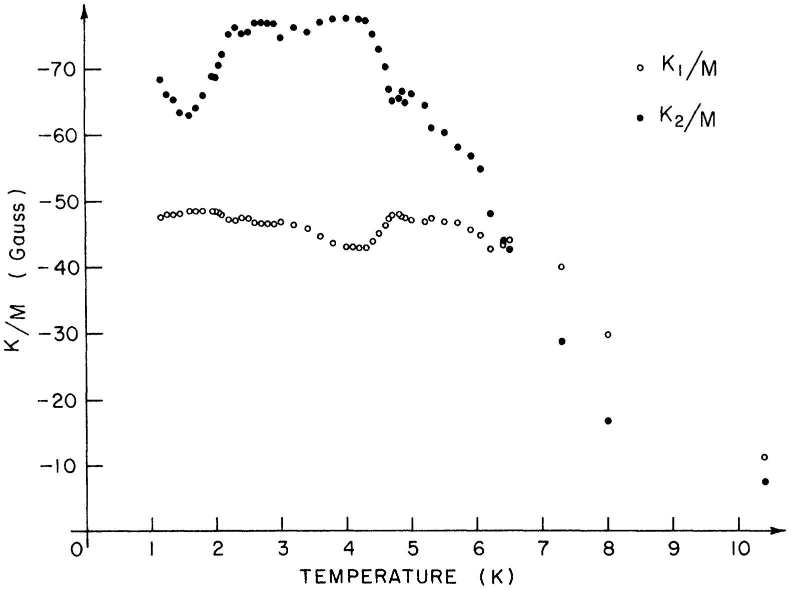

FIG. 1. Experimentally determined variation with temperature of the first, K_1/M, and second, K_2/M, cubic anisotropy constants in EuSe. The zero-field ordering temperature is 4.6 °K.

of error analysis is given in Ref. 9.

III. EXPERIMENTAL RESULTS AND DISCUSSION

The measured variation with temperature of the anisotropy constants K_1/M and K_2/M is shown in Fig. 1. The values obtained are in agreement with the previously reported values at 1.35 °K.[6] We note that there is a small bump in both K_1M and K_2/M near the zero-field ordering temperature at 2.8 °K. The very pronounced minimum in K_2/M at 1.55 °K does not correspond to any of the structure observed in either specific-heat[11] or initial susceptibility measurements.[12] For purposes of showing the total inapplicability of the Wolf single-ion model of anisotropy[7] for EuSe as extended by von Molnar,[8] we have used this theory, determining the values of b_4 and b_6 to fit K_1 and K_2 at ~ 1 °K, and calculated the "expected thermal variation" at our measuring field strength. The results are shown in Fig. 2. In the Wolf model, the contribution of exchange is approximated by replacing the field in the spin Hamiltonian by an effective field

$$\vec{H}_{eff} = \vec{H}_i + \lambda \vec{M}(\vec{H}_i, T),$$

where $\vec{H}_i$ is the internal field, $\vec{M}(\vec{H}_i, T)$ is the magnetization, and λ is the molecular-field constant. McGuire *et al*.[13] have measured the magnetization versus temperature in an applied field

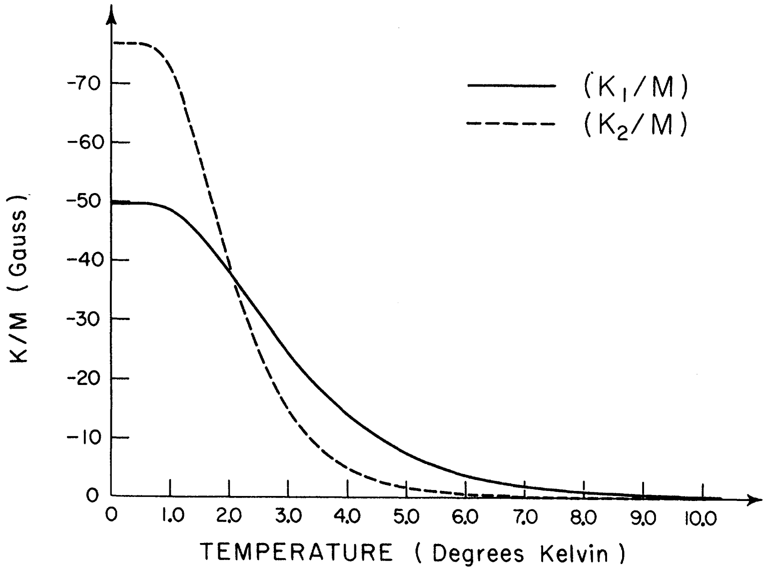

FIG. 2. Calculated variation of K_1/M and K_2/M obtained using Wolf's single-ion model (Ref. 7) and the molecular-field approximation for EuSe. The crystal-field parameters used were obtained by fitting the experimental data at our lowest temperature (1.15 °K) but are somewhat arbitrary. Comparison with Fig. 1 shows the inability of this model to describe the measured variation.

of 10 kOe. The result is a smooth ferromagnetic-like variation with a "ferromagnetic Curie temperature" of 7 °K as determined from the point of inflection. Thus, the measured paramagnetic Curie temperature $\Theta_P = 6$ °K[16] together with the molecular-field approximation represents quite well the high-field temperature variation of the magnetization. Lacking an independent determination of $\vec{M}(\vec{H}, T)$ for our samples, we have assumed that the molecular-field model will also describe the variation of $\vec{M}(\vec{H}, T)$ and hence $\vec{H}_{eff}$ at our measuring field of 8.6 kOe. The predicted exponential decrease in both K_1/M and K_2/M is in marked disagreement with the almost constant value of K_1/M observed below the ordering temperature and would not be appreciably changed by using more precise experimental values of M in the calculation. In contrast to EuO[9] and EuS,[10] the value of K_2 is greater than K_1 underscoring the basic difference between these materials. According to the magnetic phase diagram,[16] we should be well into the ferromagnetic phase at all temperatures with our measuring fields and thus expect these three compounds to give similar results. The nearly constant value of K_1/M below 6 °K is in marked contrast with the expected $K_1 \propto M^{10}$ dependence expected in cubic ferromagnetic material when $\vec{M}(T)/\vec{M}(0) \sim 1$.[19] No evidence of such behavior in K_1 is seen at our lowest temperature though the marked increase in K_2/M below 1.55 °K may indicate that the 10th-power-law dependence for K_1 would be observed at lower temperatures.

A general harmonic analysis of our data yields terms, Eq. (2), higher than the $\cos 6\varphi$ dependence of the first-order resonance equation. The amplitudes of terms in $\cos 8\varphi$ and $\cos 10\varphi$ are small but real, decreasing to zero with increasing temperature. Such terms are expected when the resonance equation is determined to second order in Δ_1 and Δ_2.[9] We have analyzed our experimental results using the second-order resonance equations and find that these terms do account for the higher harmonics observed to within the experimental uncertainty but change the value of K_2 determined by only 3% at the lowest temperature. There is no qualitative effect on the temperature dependence of either K_1 or K_2. The presence of a magnetostatic mode near the uniform precession can have a marked effect on the amplitudes $\vec{H}_{2n}$ determined from the angular dependence $\vec{H}(\varphi)$. Our use of spherical samples in the region of the cavity where the rf $\vec{H}$ field is uniform precludes this possibility and none were observed. The fewer points taken above 7 °K reflect the increasing difficulty in obtaining useful data in the region of rapidly increasing linewidth. The data shown in Fig. 1 are the result of measurements taken over a period of many days but on just one sample. Different samples prepared in different ways show the same behavior but differ in the absolute values determined.

The temperature dependence of the linewidth determined by the separation of the extrema in dP/dH with the magnetic field along a $\langle 100 \rangle$ direction is shown in Fig. 3. The linewidth is anisotropic even at our lowest temperature. The minimum values occur for $\vec{H}$ along $\langle 100 \rangle$ and $\langle 110 \rangle$ directions with a maximum value with $\vec{H}$ along $\langle 111 \rangle$. At 1.15 °K we observe $(\Delta H)_{111} \sim 1.6\,(\Delta H)_{100}$. We do not observe a simple correspondence between the angular dependence of ΔH and the resonant field $H(\varphi)$. The value of $\Delta H \sim 20$ Oe at 1.5 °K and its finite derivative $d(\Delta H)/dT$ indicate that the observed dependence is intrinsic to EuSe and is not being limited by surface roughness scattering. The change in slope of ΔH with increasing temperature of ~3.0 °K corresponds to the zero-field transition from the AFM to mixed ferrimagnetic and AFM phases suggested

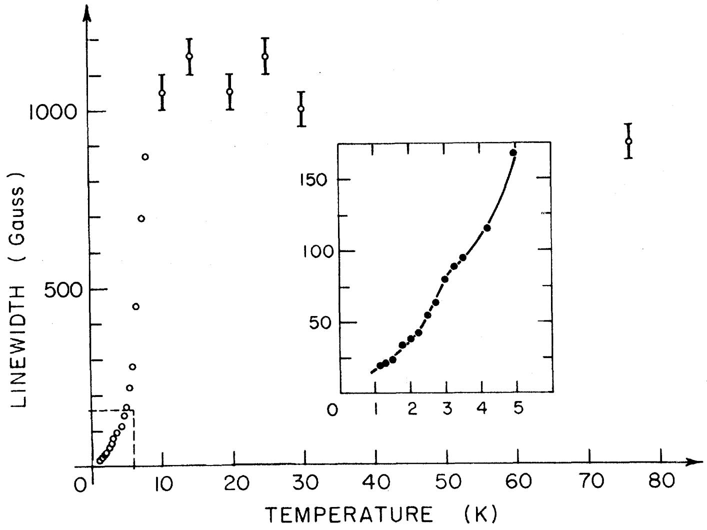

FIG. 3. Ferromagnetic resonance linewidth versus temperature determined from the half-power points and with the applied field along a $\langle 100 \rangle$ direction. The insert is an enlargement of the region shown by dashed lines and indicates the change in slope with temperature of the linewidth at 3 °K. The decrease in linewidth in going from 20 °K to 77 °K is discussed in the text.

by other authors[16] but in a field such that only the ferromagnetic phase should exist. The linewidth goes through a broad maximum of ~1100 Oe at 20 °K and decreases to 900 Oe at 77 °K. Above this temperature, it increases, but very slowly. This behavior is similar to that of an AFM in an external field sufficiently strong to largely suppress spin fluctuations near the ordering temperature. For a ferromagnet, the linewidth increases continuously with temperature as has been observed in EuS.[20] The maximum in ΔH for EuSe being an impurity effect can be ruled out by its absence in EuS. Both materials were prepared in the same manner and had the small linewidth values at low temperature after the purification by fractional distillation. The temperature variation of the anisotropy constants and the linewidth for an internal field $H_i = 4$ kOe both indicate that the existing magnetic phase diagram is an oversimplification and that the description of EuSe as a simple ferromagnet for $H_i > 2$ kOe is incomplete.

We do not, at the present time, have either a quantitive or qualitative explanation for our results. The calculation, Fig. 2, using the single-ion model[7,8] showing it not to be applicable to EuSe, does not indicate that it is in error but, more likely, the assumed purely cubic local symmetry is not satisfied. In particular, it has been shown[21] that EuSe contains domains which are very small. The situation is similar to the AFM, EuTe for which domains have also been observed[21,22] and which has fcc type-II order. The low-temperature ($T < 2.8$ °K) AFM of EuSe has also been identified as type II.[14] It has been shown for the isomorphic AFM NiO that the T domains form when the material orders magnetically and that they cannot be removed by the application of a magnetic field.[23] Similarly, theoretical studies show that the deformation tensor is uniform within a domain but changes continuously within a domain wall.[24] Finally, it has been shown from a molecular-field interpretation of T_N and Θ_P that $J_2/|J_1| \simeq -1$ where J_1 and J_2 are the first- and second-nearest-neighbor exchange interactions, respectively.[16] This predicts that EuSe should be very close to a triple point on a magnetic-phase stability diagram.[25] Thus any distortions associated with the ordering process would have an influence on the type of ordering, and processes in the domain walls themselves can contribute to the macroscopic properties of a sample.

In his paper on single-ion anisotropy, Wolf[7] considered the contribution of a distortion in the local symmetry causing an extra term of the form $D\hat{S}_\alpha^2$ to be present in the effective spin Hamiltonian where α is the direction of the distortion. It was shown that such a term does make a contribution to the first-order cubic anistropy constant when the distortion is associated with definite crystallographic directions, i.e., $\langle 111 \rangle$ or $\langle 100 \rangle$ directions, and that the temperature dependence of such contributions is not monotonic. For $S = \frac{7}{2}$, this term would have a maximum for $|M/M_0| \sim 0.95$, decreasing rapidly below and slowly above this temperature. This shows that distortion effects can have a pronounced effect on the magnitude and temperature dependence of measured anisotropy constants. It is tempting to speculate the following: (i) EuSe contains domains but with the domain walls representing an appreciable fraction of the sample volume. (ii) The distortions in the domain walls represent appreciable deviations from cubic symmetry affecting both the exchange and crystal-field parameters. (iii) The observed anisotropy energy results from the contributions of the domains and domain walls, but with the domain-wall region characterized by lower symmetry than cubic.

IV. CONCLUSIONS

We have shown that the first- and second-order cubic anisotropy constants in EuSe are not described by a single-ion mechanism. The almost temperature-independent behavior of K_1/M below the ordering temperature is in marked contrast to that observed in EuO and EuS. The unexpected behavior of the anistropy constants and of the linewidth for an internal field $\bar{H}_i = 4$ kOe shows the simple magnetic-phase diagram for EuSe to be an oversimplification. We have speculated that domains and domain walls are important contributors to the anistropy energy. It would be extremely interesting to repeat this experiment on single-domain samples prepared by cooling through the ordering temperature under uniaxial stress.

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*Present address: Department of Physics, Southwestern State College, Weatherford, Okla. 73090.

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Hall Effect in the Presence of Strong Spin-Disorder Scattering

W. F. Brinkman and T. M. Rice
Bell Telephone Laboratories, Murray Hill, New Jersey 07974

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The Hall mobility μ_H of a single hole in a Mott-Hubbard band of a magnetic insulator is considered using a path formulation of the atomic limit of the Hubbard model. It is shown that within a generalization of the retraceable-path approximation, the Hall mobility and the drift mobility μ_D are essentially equal at high temperatures compared with the bandwidth, but that the Hall mobility becomes small compared to the drift mobility as the temperature is lowered. The ratio μ_H/μ_D becomes proportional to the ratio of the temperature to the bandwidth at low temperatures.

I. INTRODUCTION

The theory of the Hall effect in the presence of strong scattering is a difficult problem. A general discussion of the problem has been given by Herring[1] and by Kubo.[2] The specific cases of liquid metals have been examined by Springer[3] and by Allgaier[4] and of small polarons by Friedman and Holstein[5] and by Emin and Holstein.[6] In this paper we shall examine the case of an electron or hole in a magnetic semiconductor which is strongly coupled to and scattered by spin waves. An excellent and detailed review of the experimental situation in magnetic semiconductors such as NiO, CoO, Fe_2O_3, and MnO has been given recently by Bosman and van Daal.[7] These authors conclude that the free carriers in most of these materials are probably not small polarons and they point out the importance of a theoretical understanding of transport properties and in particular the Hall effect in the presence of strong spin-disorder scattering.

In this paper we shall examine the Hall effect for an extra carrier (electron or hole) in an otherwise half-filled band in the atomic limit of the Hubbard model. Langreth[8] has examined the Hall coefficient using Hubbard's approximate treatment of his model.[9] However, this treatment ignores the strong coupling between an extra carrier and the localized spins. This coupling is so strong in the atomic limit that as shown recently by Ohata and Kubo[10] and by the present authors,[11] the motion of an extra carrier is more properly considered as a diffusion or Brownian motion through the lattice rather than a propagating or wavelike motion. The former authors calculated the first few moments of the frequency-dependent conductivity and by fitting a Gaussian or a Lorentzian form to the conductivity-obtained values for the dc mobility. The latter authors used a technique due to Nagaoka[12] of representing the problem in terms of walks on a lattice to examine the density of states for the extra carrier. They found that an approximation in which only walks with no closed loops are included gave a very reasonable form for the density of states in