Electrical Properties of Na₃Cu₄S₄, a Mixed-Valence One-Dimensional Metal

ZBIGNIEW PEPLINSKI,[1a] DAVID B. BROWN,*[1a] TIMOTHY WATT,[1a] WILLIAM E. HATFIELD,[1b]
and PETER DAY[1c]

Four probe electrical conductivity measurements from 15 to 300 K demonstrate that the mixed-valence compound Na₃Cu₄S₄ is metallic. Measurements on single crystals reveal that the conductivity is highly anisotropic, with enhanced conductivity parallel to the crystal needle axis, corresponding to pseudo-one-dimensional $[Cu_4S_4^{3-}]_\infty$ columns in the structure. For single crystals, $\sigma_\parallel$ increases from 15000 Ω^{-1} cm^{-1} at 300 K to 300000 Ω^{-1} cm^{-1} at 15 K. A small, temperature-independent magnetic susceptibility is consistent with metallic behavior. Diffuse-reflectance spectra support the formulation of this compound as a class 3B mixed-valence S²⁻/S⁻ solid.

Introduction

In 1952 Rudorff, Schwarz, and Walter reported a remarkable series of mixed-valence solids.[2] Heating mixtures of copper, sulfur, and alkali carbonates in a muffle furnace to temperatures of 700–1000 °C gave shiny blue-black solids with compositions indicating the formal incorporation of one copper(II) ion and two, three, or seven copper(I) ions, e.g., Na₂Cu₃S₃, KCu₄S₃, and K₃Cu₈S₆. Recently, several isostructural analogues of KCu₄S₃ have been reported.[2,3,4] Intrigued by the original report of high electrical conductivity in these materials, we initiated studies of their structural, electrical, and magnetic properties, and we have recently demonstrated[5] that KCu₄S₃ is a two-dimensional metal. In contrast to the platelike crystals of the two-dimensional KCu₄S₃, Na₂Cu₃S₃ was reported to form needlelike crystals. Although crystal morphology is not a perfect guide to structure, it seemed possible that Na₂Cu₃S₃ might be one dimensional, both structurally and electrically. While our studies of this material were in progress, Burschka reported[6] its structure and demonstrated that its actual composition is Na₃Cu₄S₄, nominally a Cu^{I}Cu^{I}Cu^{I}Cu^{II} mixed-valence compound. The structure consists of one-dimensional columns, with [Cu₄S₄]³⁻ chains separated by sodium ions. Although there are two crystallographically distinct copper sites, both sites involve trigonal coordination by sulfur, with comparable Cu–S bond distances for the two copper ions. Thus, as in KCu₄S₃, there are no distinct Cu(I) and Cu(II) ions; e.g., the material is probably best described as delocalized class 3B mixed-valence compound.[7] We report here that the electrical properties of Na₃Cu₄S₄ are totally consistent with this formulation.

Experimental Section

Preparation of Na₃Cu₄S₄. Na₃Cu₄S₄ was prepared as described in the literature.[2,6] Better crystals could be obtained by heating mixtures of copper powder, sulfur, and sodium carbonate in a nitrogen atmosphere at approximately 500–550 °C for 2 h with a tube furnace. Anal. Calcd for Na₃Cu₄S₄: Na, 15.28; Cu 56.31; S, 28.41. Found: Na, 15.90; Cu, 56.16; S, 27.96. Sodium was analyzed by atomic absorption spectroscopy, and copper was analyzed by EDTA titration

with murexide indicator following decomposition in aqua regia. Sulfur determinations were performed by Schwarzkopf Analytical Laboratories.

Diffuse-Reflectance Spectra. Samples were finely ground and dispersed in MgO. Diffuse-reflectance spectra were measured with a Perkin-Elmer 330 spectrophotometer equipped with a reflectance attachment using MgO as the reference.

Magnetic Susceptibilities. Magnetic susceptibilities of randomly oriented crystals were measured as described previously[8] with a conventional Faraday balance calibrated with Hg[Co(NCS)₄].[9] Diamagnetic corrections for the constituent atoms were made with use of values tabulated by Mulay.[10]

Electrical Conductivity. Four-probe dc conductivities of polycrystalline compactions were measured with the van der Pauw technique.[11] Pellets (6.3-mm diameter, typically 1 mm thick) were generally pressed at ca. 80000 psi, although measured conductivities were not sensitive to the pressure used in pellet preparation. A locally designed Teflon sample holder with four spring-loaded stainless-steel pressure contacts symmetrically disposed at the perimeter of the pellet was used for these measurements. Currents were imposed on a pair of adjacent probes by a Keithley Model 225 current source, and the voltage drop at the other pair of probes was measured with a Keithley Model 147 nanovoltmeter. A 90° rotation of the leads was used to ensure that results were not sensitive to probe positioning. Conductivities were then calibrated from the relationship

$$\sigma = ((\ln 2)/\pi t)(1/R) = 0.2206(I/tV)$$

where σ is the conductivity (Ω^{-1} cm^{-1}), R the resistance (Ω), I the imposed current, V the measured voltage, and t the pellet thickness (cm). Low temperatures were obtained by suspending the sample holder in the Faraday balance shroud of a Model CS-202 Displex closed-cycle helium refrigerator with a Model APD-E temperature controller manufactured by Air Products and Chemicals, Inc., Allentown, PA. With this system measurements could be made from 13 to 300 K.

Single-crystal conductivity measurements at room temperature were made with both pressure contacts and silver paint contacts. In either case, electrical connections to the crystal were positioned with joy-stick micromanipulators manufactured by the Micromanipulator Co., Escondido, CA. Single crystals for variable-temperature conductivity measurements were mounted in integrated circuit cans.[12] After the top of the can was ground off, the crystal was attached to the central chip with double-sided Scotch tape. Silver paint, prepared by diluting Dupont Conductor No. 4929 with hexyl acetate, was painted on the ends of the crystal and two thin strips of silver were painted across

(1) (a) University of Vermont. (b) The University of North Carolina. (c) Oxford University.
(2) Rudorff, W.; Schwarz, H. G.; Walter, M. *Z. Anorg. Allg. Chem.* **1952,** *269,* 141. (The compound "Na₂Cu₃S₃" had been reported: Schneider, R. *J. Prakt. Chem.* **1865,** *108,* 16.)
(3) Klepp, K.; Boller, H.; Völlenkle, H. *Monatsh. Chem.* **1980,** *111,* 727.
(4) Burschka, C. *Z. Anorg. Allg. Chem.* **1980,** *463,* 65.
(5) Brown, D. B.; Zubieta, J. A.; Vella, P. A.; Wrobleski, J. T.; Watt, T.; Hatfield, W. E.; Day, P. *Inorg. Chem.* **1980,** *19,* 1945.
(6) Burschka, C. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1979,** *34B,* 396.
(7) Robin, M. B.; Day, P. *Adv. Inorg. Chem. Radiochem.* **1967,** *10,* 248.
(8) Dziobkowski, C. T.; Wrobleski, J. T.; Brown, D. B. *Inorg. Chem.* **1981,** *20,* 671.
(9) Brown, D. B.; Crawford, V. H.; Hall, J. W.; Hatfield, W. E. *J. Phys. Chem.* **1977,** *81,* 1303.
(10) Mulay, L. N. "Theory and Applications of Molecular Paramagnetism"; Boudreaux, E. A., Mulay, L. N., Eds.; Wiley: New York, 1976; pp 494–495.
(11) van der Pauw, L. J. *Philips Res. Rep.* **1958,** *13,* 1.
(12) Phillips, T. E.; Anderson, J. R.; Schramm, C. J.; Hoffman, B. M. *Rev. Sci. Instrum.* **1979,** *50,* 263.

the crystal, approximately one-third of the way from each end. Connections to the integrated circuit terminals were achieved by painting a silver ribbon to the crystal contacts. Current was imposed through the outer contacts and the voltage drop measured between the inner two contacts. Crystal dimensions and voltage probe separations were measured by microscopic comparison to the scale of a hemacytometer counting stage which was ruled to 0.02 mm. Conductivities were calculated from the relationship $\sigma = (l/A)(I/V)$, where l is the voltage probe separation, A the cross-sectional area of the crystal, and I and V the current and voltage, respectively. Variable-temperature measurements were made by suspending the integrated circuit can in the shroud of the closed-cycle helium refrigerator, as described above for the compaction measurements. Ohmic behavior was verified in all cases.

Results and Discussion

The original preparation[2] of Na$_3$Cu$_4$S$_4$ involved placing sodium carbonate, copper, and sulfur in a double-crucible arrangement and heating in a muffle furnace to 700–1000 °C for 1–3 h. Minute crystals of the compound are formed in this way, but alterations in both the relative amount of reactants and the reaction conditions seemed to have no consistent effect upon the quality of the crystals produced. We have found that significantly larger single crystals—necessary for the conductivity measurements—may be formed by carrying out the reaction in an inert atmosphere (N$_2$) in a tube furnace at somewhat lower temperatures (ca. 550 °C). Temperature control is rather important. If the reaction temperature is less than 500 °C, the product is frequently contaminated by CuS. The presence of CuS may be detected visually since it crystallizes as blue plates rather than as the blue-black needles of Na$_3$Cu$_4$S$_4$. It is further reflected in the analytical results (high % Cu) and the room-temperature conductivity (higher than that of Na$_3$Cu$_4$S$_4$ by a factor of ca. 10). Higher reaction temperatures generally give pure Na$_3$-Cu$_4$S$_4$ but as a powder rather than as crystals. This behavior contrasts with that observed in analogous preparations using potassium or lithium salts in place of sodium carbonate. Reactions using K$_2$CO$_3$ produce CuS as the high-temperature (>1000 °C) product, whereas the reactions with Li$_2$CO$_3$ give Cu$_{1.8}$S as the only identifiable copper sulfide.[13]

Although crystals of Na$_3$Cu$_4$S$_4$ are apparently stable if stored in dry oxygen or under water, in moist air they slowly lose their metallic luster and develop an insulating surface coating. Consequently, all measurements reported here were made on fresh preparations of the material which had been stored in a nitrogen atmosphere.

In the temperature range of 100–300 K, Na$_3$Cu$_4$S$_4$ exhibits a temperature-independent paramagnetism of ca. 150 × 10^{-6} emu/mol. This value is comparable to that found for KCu$_4$S$_3$ and is the behavior expected for a metallic system.[14] Below 100 K the compound exhibits Curie-like behavior, presumably as a consequence of the presence of a small amount of paramagnetic impurity.

The electrical conductivity for pressed pellets of Na$_3$Cu$_4$S$_4$ has been measured with the four-probe van der Pauw technique.[11] For samples which we believe to be free of CuS contamination, the room-temperature conductivity is consistently near 300 Ω^{-1} cm^{-1}. Thus, for five separate preparations which gave both the correct crystal morphology and copper analyses, the range of conductivity values was 290–350 Ω^{-1} cm^{-1}, with an average $\sigma = 328 \pm 35$ Ω^{-1} cm^{-1}.

Rudorff et al.[2] reported pressed-pellet room-temperature electrical conductivities of 80 Ω^{-1} cm^{-1} for Na$_3$Cu$_4$S$_4$, 70 Ω^{-1} cm^{-1} for K$_3$Cu$_8$S$_6$, and 40 Ω^{-1} cm^{-1} for KCu$_4$S$_3$. By contrast, we find values of 4000 Ω^{-1} cm^{-1} for KCu$_4$S$_3$[5] and 300 Ω^{-1} cm^{-1}

(13) Peplinski, Z.; Brown, D. B., unpublished observations.
(14) Schramm, C. J.; Scaringe, R. P.; Stojakovic, D. R.; Hoffman, B. M.; Ibers, J. A.; Marks, T. J. *J. Am. Chem. Soc.* **1980**, *102*, 6702 and references therein.

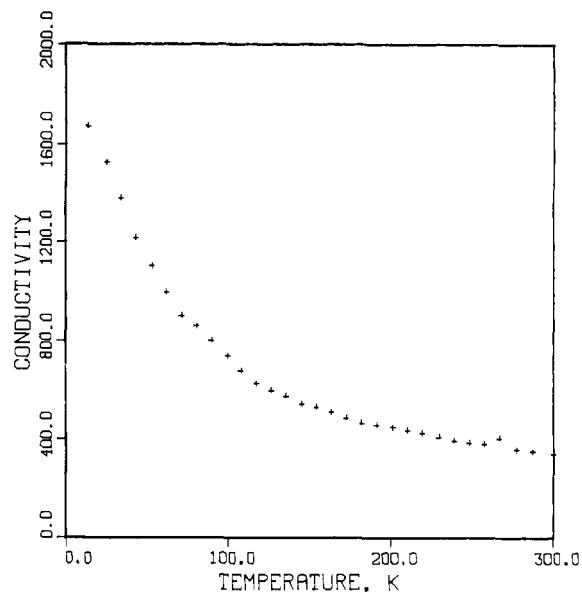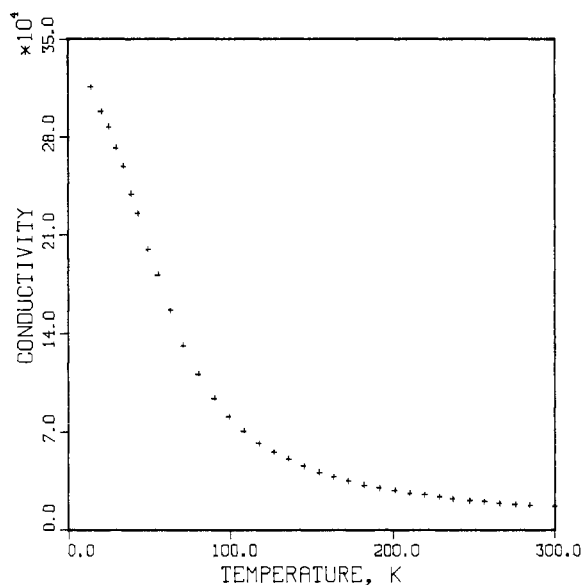**Figure 1.** Electrical conductivity (Ω^{-1} cm^{-1}) as a function of temperature for a pressed pellet of Na$_3$Cu$_4$S$_4$.

for Na$_3$Cu$_4$S$_4$. Although not stated explicitly, it is probable that Rudorff et al. used a two-probe measurement technique. In that case, the measured resistance is the sum of the inherent sample resistance plus the contact resistance. For such highly conducting materials, the contact resistance will dominate. Thus the low values for the conductivity which were reported, as well as the lack of differentiation among the various compounds, may be understood as the consequence of a two-probe measurement technique.

The temperature dependence of the pressed-pellet conductivity is that of a metal. Upon cooling of the sample (Figure 1), the conductivity increases monotonically, reaching values of ca. 1500 Ω^{-1} cm^{-1} at 15 K. This increase—a factor of ca. 4–5—is rather small. We believe that it is not an inherent property of the compound but rather an artifact caused by the use of pressed pellets. Interparticle contact resistances may represent a significant contribution to the total resistance for pressed pellets. To the extent that these terms are independent of temperature, they will mask the true dependence of the sample conductivity upon temperature.

Na$_3$Cu$_4$S$_4$ is structurally a pseudo-one-dimensional compound,[6] and its electrical properties should be correspondingly anisotropic. Consequently, we have measured the conductivity of single crystals of Na$_3$Cu$_4$S$_4$. The crystals are needlelike, with a typical length of 1 mm and rectangular cross section of 0.03 × 0.04 mm^2. Because of these small dimensions, it has only been possible to measure the conductivity parallel to the needle axis, which corresponds to the direction of the one-dimensional [Cu$_4$S$_4$$^{3-}$]$_\infty$ columns. Although crystal dimensions were estimated by optical comparison to a scale ruled to 0.02 mm, the small size of the crystals means that there is a relatively large uncertainty in these measurements. Since the calculation of the conductivity depends upon the cross-sectional area of the crystal, there will be a relatively large uncertainty in the absolute value of the single-crystal conductivity. For ten separate crystals from two different preparations, the average single-crystal conductivity was $\sigma_\parallel = 15\,200 \pm 3000$ Ω^{-1} cm^{-1}. The range for six crystals from one preparation was 12 500–18 700 Ω^{-1} cm^{-1}, and we attribute this rather large spread to the difficulty in measuring the crystal dimensions precisely.

As for the pressed pellets, the temperature dependence of the conductivity of single crystals (Figure 2) is that of a metal, the conductivity increasing smoothly as the temperature is

Figure 2. Electrical conductivity (Ω^{-1} cm^{-1}) as a function of temperature for a single crystal of $Na_3Cu_4S_4$. Four-probe conductivities were measured parallel to the needle axis.

Figure 3. Resistivity (Ω cm) as a function of temperature for a single crystal of $Na_3Cu_4S_4$. The solid curve is the best straight-line fit to the data in the range 80–300 K.

decreased. In this case, however, the curve is steeper, and the conductivity increases by a factor of ca. 20 (from 15 000 to 300 000 Ω^{-1} cm^{-1}) upon cooling from 300 to 15 K. This tends to substantiate our suggestion that the gentle temperature dependence observed with pressed pellets results from interparticle resistance.

These data demonstrate that $Na_3Cu_4S_4$ is a pseudo-one-dimensional metal. The single-crystal conductivity parallel to the one-dimensional columns of the crystal is greater, by a factor of approximately 50, than the bulk conductivity. Such a difference is common for low-dimensional materials and is a reflection of both the inherent anisotropy of the material and the interparticle resistance in the pressed pellet measurements. The conductivity cannot be strictly described as one dimensional, since there is presumably finite electron mobility in all directions, although it would extend for only atomic dimensions perpendicular to the column axis. These columns are separated from each other by insulating regions occupied by sodium ions, and consequently on the macroscopic level the conductivity will be significantly anisotropic.

The plots of conductivity vs. temperature for both single crystals and pressed pellets of $Na_3Cu_4S_4$ exhibit an apparent inflection point at ca. 40 K, and there is some suggestion that the conductivity will level off below the minimum temperature (13 K) accessible to us. Nonetheless, above ca. 80 K plots of resistivity vs. temperature are linear (Figure 3). This is behavior typical of simple metals and may be contrasted to the case of molecular metals where the resistivity varies approximately as the square of the temperature.[14] Attempts to model the data with use of an equation of the form $\rho = A + BT^2$ did not lead to acceptable agreement between calculated and experimental values.

A large number of copper sulfide phases are known,[5] including the obviously mixed-valence compounds $Cu_{2-x}S$. Although a range of stoichiometries are apparently possible, the discrete phases Cu_2S (chalococite), $Cu_{1.96}S$ (djurleite), $Cu_{1.8}S$ (digenite), and $Cu_{1.75}S$ (anilite) have been recognized. Even CuS, which is nominally a simple Cu(II) compound, is mixed valent since discrete S_2 groups (formally S_2^{2-}) are present. Wells[15] has formulated this compound as
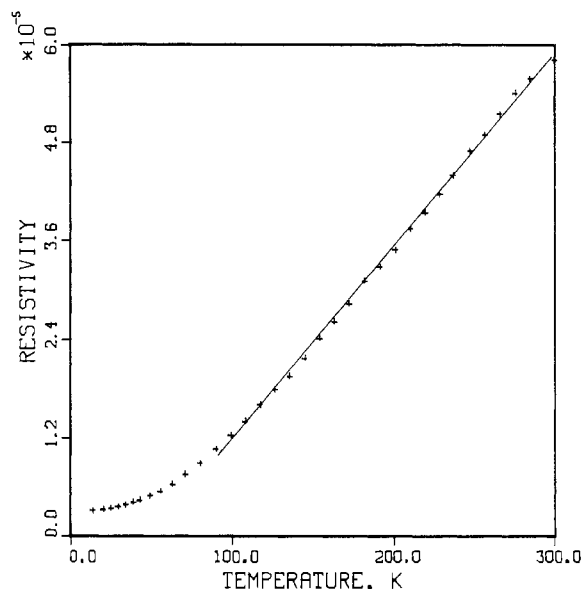
$Cu^I_4Cu^{II}_2(S_2^{2-})_2(S^{2-})_2$. Several of these phases exhibit metallic, or semi-metallic, electrical behavior.

$Na_3Cu_4S_4$ has Cu–Cu distances[6] which satisfy the Goodenough criterion[16] for high mobility collective electrons. The mixed-valence nature of this compound will lead to partially filled bands, and in consequence the high metallic conductivity seems explicable. Although $Na_3Cu_4S_4$ has two distinct Cu sites, both involve trigonal coordination by sulfur with very similar bond distances. Clearly, there is no way to attribute these sites to distinct oxidation states of Cu, and $Na_3Cu_4S_4$ is appropriately described as a Robin and Day class 3B mixed-valence compound. On this basis alone its metallic conductivity may be predicted. Similarly, although there are two crystallographically distinct sulfur sites, their environments are comparable and, to a first approximation, may be considered equivalent.

Although we have described these mixed-valence compounds as Cu^ICu^{II} species, there is recent evidence that suggests that the mixed valency resides in the sulfur rather than copper. In particular, X-ray photoelectron spectroscopy has demonstrated that all known copper sulfides—including KCu_4S_3 and $Na_3Cu_4S_4$—contain Cu(I) only, with no evidence for either Cu(II) or intermediate oxidation states.[17,18] Thus, Folmer and Jellinek[7] reformulate CuS as $Cu^+_3(S_2)^{2-}S^-$ and KCu_4S_3 as $K^+Cu^+_4(S^{2-})_2S^-$. With this scheme, $Na_3Cu_4S_4$ must then be formulated as $Na^+_3Cu^+_4(S^{2-})_3S^-$. Because of the low electronegativity of sulfur and the relatively high electronegativity of copper, the copper d levels fall within the valence band of sulfur. This results in a reduction of Cu^{2+} to Cu^+ with a concurrent partial depopulation of the sulfur valence band.[19,20] It is this partially filled valence band—formally mixed-valence sulfur—which is responsible for the metallic conductivity of $Na_3Cu_4S_4$. Although this recent work emphasizes that it is necessary to describe these complexes differently (that is, as mixed-valence sulfur compounds rather than as mixed-valence copper compounds), it does not alter any fundamental conclusions. These are still class 3B mixed-valence compounds, with no distinguishable "S^{2-}" and "S^-"

(15) Wells, A. F. "Structural Inorganic Chemistry", 3rd ed.; Oxford University Press: London, 1962; p 883.

(16) Goodenough, J. B. "Magnetism and the Chemical Bond"; Interscience: New York, 1963.
(17) Folmer, J. C. W.; Jellinek, F. *J. Less-Common Met.* **1980**, *76*, 153.
(18) Rupp, H.; Weser, U. *Bioinorg. Chem.* **1976**, *6*, 45.
(19) Jellinek, F. *MTP Int. Rev. Sci., Inorg. Chem., Ser. One* **1972**, *5*, 339.
(20) Folmer, J. C. W. Thesis, University of Groningen, 1981.

sites and as such are expected to exhibit metallic conductivity.

Diffuse-reflectance spectra of $Na_3Cu_4S_4$ are consistent with this formulation. The spectra exhibit a reflectivity peak near 35 000 cm^{-1}, a very broad shoulder around 20 000 cm^{-1}, and a smeared out edge at 12–14 000 cm^{-1} which might be ascribed to the plasma edge. A reflectivity peak, ascribable to the 3d → 4s transition of Cu(I), often appears near 35 000 cm^{-1} in Cu(I) complexes. The observation of such a peak in $Na_3Cu_4S_4$ supports the photoelectron spectroscopy work by suggesting that $Na_3Cu_4S_4$ is a discrete Cu(I) complex.

A large number of alkali–copper–sulfide phases are now known, and it appears likely that all have interesting and unusual electrical properties. Furthermore, it appears that some of these materials are subject to chemical modification. We have, for example, prepared mixed Na/K analogues, but it is not yet clear whether these represent distinct phases or simply substitutional doping of KCu_4S_3 and $Na_3Cu_4S_4$. We will report on other alkali copper sulfides at a later date.

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Contribution from the Dipartimento di Fisica, Università della Calabria, Cosenza, Italy, and Institute for Theoretical Physics, Free University of Berlin, 1000 Berlin 33, West Germany

Isolated Noble-Metal Atoms in a Neon Matrix

STEFANO OSSICINI[†] and FRANK FORSTMANN*

By a pseudopotential method, the perturbation of the outer electronic s and p levels of Cu, Ag, and Au atoms by a Ne matrix is calculated. It is concluded that for Cu and Au the trapping site consists of three vacancies. Two sites of three and four vacancies give the two different "triplets" in the absorption spectrum of Ag.

Introduction

The optical spectra of Cu, Ag, and Au atoms isolated in a Ne matrix have been recently reported.[1–4] These systems have also been studied by ESR[5] and MCD.[3] The results of the experiments can be summarized as follows:

(a) Cu and Au atoms show three absorption lines, whereas for Ag five lines are observed, which are interpreted as two, partly overlapping triplets originating from Ag at two different trapping sites.[1]

(b) ESR experiments[5] show that Cu and Au atoms occupy multiple sites and that these atoms perhaps replace two or three atoms in each site.

The investigations using a neon matrix have to be compared with the analogous systems in argon, krypton, and xenon matrices.[6–19] The absorption spectra of Cu, Ag, and Au isolated in Ar, Kr, and Xe matrices consist typically of three absorption lines, generally blue shifted, compared to the two lines in the gas phase. In these cases it has been convincingly shown that careful annealing after deposition of the matrix leads to a single well-defined site of the impurity with very sharp absorption lines.[16] It was shown recently[18a] that for Ag in Kr UV irradiation can produce a secondary trapping site, which is also found in freshly deposited Ag/Kr systems, but annealing restores the unique well-defined matrix cage.[18a] For Ag in Ne, annealing leaves always two separate sites.[1] Also ESR[5] studies of these atoms in Ar, Kr, and Xe are in agreement with the optical results and indicate a single, uniform trapping site, most likely the substitutional site.

We have recently developed a pseudopotential method[20,21] for calculating the shifts of the outer s and p levels of isolated atoms in rare-gas matrices and so the transition energies. With this model the measured blue shifts of the absorption lines for Cu, Ag, and Au in Ar, Kr, and Xe matrices were derived for substitutional sites.[20] The situation of Ag in Ne is similar to the case of isolated alkali atoms in rare-gas matrices; for these

atoms, for example Na in Ar, we clearly see two triplets, which are ascribed to Na in two different trapping sites.[22] By our pseudopotential method we have concluded that the different trapping sites for the alkali atoms are a metastable site of three vacancies and a stable trapping site of four vacancies.[21] In this work we analyze the matrix perturbation on the optical absorption spectra of Cu, Ag, and Au atoms in a Ne matrix.

The Pseudopotential and the Matrix Cage

We use the method developed in previous works.[20] We calculate with this model the energy levels of the metal atoms perturbed by rare-gas neighbors. Our Hamiltonian for the metal outer electrons is given by eq 1 with T as the kinetic

$$\mathcal{H}\Psi\rangle = (T + V_A + \sum_N V_N)\Psi\rangle = E\Psi\rangle \qquad (1)$$

energy, V_A the potential of the guest atom including the core

(1) D. M. Gruen and J. K. Bates, *Inorg. Chem.*, **16**, 2450 (1977).
(2) D. Leutloff, Thesis, Technische Universität Berlin, 1977.
(3) S. Armstrong, R. Grinter, and June McCombie, to be submitted for publication.
(4) H. Abe, to be submitted for publication.
(5) P. H. Kasai and D. McLeod, *J. Chem. Phys.*, **55**, 1566 (1971).
(6) J. S. Shirk and A. M. Bass, *J. Chem. Phys.*, **49**, 5156 (1968).
(7) L. Brewer, B. A. King, J. L. Wang, B. Meyer, and G. F. Moore, *J. Chem. Phys.*, **49**, 5209 (1968).
(8) L. Brewer and B. A. King, *J. Chem. Phys.*, **55**, 84 (1970).
(9) D. M. Mann and H. P. Broida, *J. Chem. Phys.*, **55**, 84 (1971).
(10) D. H. W. Carstens, W. Brashear, D. R. Eslinger, and D. M. Gruen, *Appl. Spectrosc.*, **26**, 184 (1972).
(11) F. Schoch and E. Kay, *J. Chem. Phys.*, **59**, 718 (1973).
(12) D. M. Gruen, S. L. Gaudioso, R. L. McBeth, and J. L. Lerner, *J. Chem. Phys.*, **60**, 89 (1974).
(13) W. Schulze, D. M. Kolb, and H. Gerischer, *J. Chem. Soc., Faraday Trans. 2*, **71**, 1763 (1975).
(14) D. M. Kolb and W. Schulze, *J. Chem. Phys.*, **64**, 2552 (1976).
(15) J. K. Bates and D. M. Gruen, *Rev. Sci. Instrum.*, **47**, 1506 (1976).
(16) F. Forstmann, D. M. Kolb, D. Leutloff, and W. Schulze, *J. Chem. Phys.*, **66**, 2806 (1977).
(17) M. Moskovits and J. E. Hulse, *J. Chem. Phys.*, **67**, 4271 (1977).
(18) (a) G. A. Ozin and H. Huber, *Inorg. Chem.*, **17**, 155 (1978); (b) S. A. Mitchell, J. Farrell, G. A. Kenney-Wallace, and G. A. Ozin, *J. Am. Chem. Soc.*, **102**, 7702 (1980).
(19) T. Welker and T. P. Martin, *J. Chem. Phys.*, **70**, 5683 (1979).
(20) F. Forstmann and S. Ossicini, *J. Chem. Phys.*, **73**, 5997 (1980).
(21) S. Ossicini and F. Forstmann, *J. Chem. Phys.*, **75**, 2076 (1981).
(22) L. C. Balling, M. D. Havey, and J. F. Dawson, *J. Chem. Phys.*, **69**, 1670 (1978).

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* To whom correspondence should be addressed at the Free University of Berlin.
† Università della Calabria.